Processing and optimising the mechanical and physical properties of natural fibre reinforced polypropylene composites

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Abstract

Although natural fibre thermoplastic composites have attractive advantages like light weight, low cost and the ecological friendly behaviour, the problems facing their processing the production of these composites are still hindering their spread in market. These problems lie in the optimisation of fibre and matrix treatments for enhanced coupling, technology adaptation, compromise of compounding and processing parameters and lack of data about the effect of functional additives. This work focuses on the polypropylene flax system as a case study. The objective is to follow along the complete processing line in order to optimise the final mechanical and selected physical properties like water absorption, etc.

The first topic in this work is the concept of using different treatments for both fibre and polymer matrix. Fibre is treated by alkalinisation alone or combined with trimethoxy vinylsylan or combined with acrylic acid. Polypropylene treatment is by trimethoxy vinylsylan or maleic anhydride grafted polypropylene or acrylic acid grafted polypropylene. However, the rule of adding the appropriate amount and type of coupling agent is still controversial. After finding the optimum treatment recipe, the second topic is to study the extrusion compounding parameters. Different extruder configurations and speeds are controlled in order to observe their effects on the development of fibre size as well as the end mechanical properties. The extruded composites are then pellitised and further processed by injection moulding. Third topic is the optimisation of the injection moulding parameters (Temperature, injection pressure, Mould temperature and screw speed) regarding mechanical properties and flow characteristics. Final topic is the effect of the functional additives. Improving the impact strength of the natural fibre thermoplastic composites is an essential issue. Therefore different ways are tried namely plasticizer (Triacetin up to 20 wt%), elastomeric rubber (Ethylene propylene diene monomer up to 10 wt%) and hybridisation of flax with the high cellulosic nettle fibre. In the same way, the effect of different flame retardants (Inorganic hydrates, halogenated, halogen-free intumescent) and synergists (antimony trioxide and nanoclays) is studied with 30 and 50% flax/PP composites. Another question is to optimise the aluminium trihydrate amount with polypropylene flax composites with respect to the flame retardance level as well as the mechanical properties.

The results of the four topics show that the optimum treatment of flax and polypropylene is by alkalinisation and maleic anhydride grafted polypropylene respectively. A table of coupling optimum amounts is defined with respect to the desired property. Secondly, the use of special elements of multi process element and teeth element has positive effects regarding the mechanical properties. Fibre size is then statistically described by Weibull function. Thirdly, fibre morphology, mould temperature, measured temperature and injection pressure are significant on the mechanical properties and flowability. An empirical model is established for the fibre content distribution. Finally, nettle fibres show better impact strength improvement compared to triacetin and EPDM. While for flame retardants, ammonium polyphosphate is the most eligible whereas mineral aluminium trihydrate is optimised at just content of 40% keeping the same high flame retardance level.

Keywords: Natural fibre, Polypropylene, Extrusion, Kneading, Characterisation.

Abstrakt

Naturfaserverstärkte thermoplastische Verbundwerkstoffe weisen sehr attraktive Vorteile auf. Diese sind z.B. ein geringes Gewicht, geringere Kosten und ihren ökologisch neutralen Footprint. Trotzdem behindern die Probleme, die bei der Verarbeitung des Naturfaserverbundmaterials auftreten, eine mögliche Verbreitung im Composite-Markt. Diese Probleme treten häufig bei den Optimierungsvorgängen der Behandlungen von Faser/Matrix Kopplungen zur Verbesserung der der Faser/Matrix Haftung auf. Mögliche Ansätze zur Technologieanpassung und zur Ermittlung optimierte Parameter bei der Kompoundierung und Verarbeitung stellen ebenfalls große Herausforderungen dar. Dazu kommen die fehlenden Informationen bezüglich der Einflüsse der funktionalen Additive der Verarbeitungstechniken und der resultierenden Verbundeigenschaften. Diese müssen angedeutet werden, um die Notwendigkeit dieses Problems besser zu verstehen und zu überwinden. Die vorliegende Arbeit thematisiert das Polypropylen-Flachs-System als Fallstudie und ist in vier Teile bzw. Themen gegliedert. Das Ziel ist die gezielte Optimierung ausgewählter mechanischer und physikalischer Eigenschaften des Endprodukts.

Das erste Thema in dieser Arbeit beschäftigt sich mit den verschiedenen Behandlungen der Faser und Polymermatrix. Die Faserbehandlung wurde bisher entweder nur durch Alkalisation oder auch in Kombination mit Trimethoxy vinylsylan oder Acrylsäure durchgeführt. Zur Veredelung der Polypropylen Matrix wurde sie mit trimethoxy vinylsylan, durch mit Maleinsäureanhydrid gepfropftes Polypropylen oder mit durch Acrylsäure gepfropften Polypropylen behandelt. Allerdings ist in der Regel die passenden Menge und Art des Kopplungsmittels umstritten. Nachdem die optimale Mischung gefunden wurde, wird darauf aufbauend die Untersuchung der Kompoundierungsparameter bei der Extrusion als zweites Thema dieser Arbeit betrachtet. Verschiedene Extruderkonfigurationen und Schneckengeschwindigkeiten (Drehzahlen) wurden in Bezug auf ihre Auswirkung auf die Fasergröße und die resultierenden mechanischen Eigenschaften untersucht.

Der Fokus des dritten Themas liegt auf der Optimierung der Spritzgießparameter, wie z.B. der Schmelztemperatur, dem Einspritzdruck, der Werkzeugtemperatur und der Schneckendrehzahl in Bezug auf die mechanischen Eigenschaften und das Fließverhalten. Der letzte Teil dieser Arbeit widmet sich der Untersuchung des Einflusses der funktionalen Additive auf den Faserverbund. Aufgrund der hohen Bedeutung des Impaktverhaltens des thermoplastischen Faserverbundes wurden unterschiedliche Methoden untersucht, um die Schlagzähigkeit zu verbessern. Als Beispiel zu nennen sind Weichmacher (Triacetin bis zu 20 Gew.-%), Elastomer (Ethylen-Propylen-Dien-Monomer bis zu 10 Gew.-%) sowie die Hybridisierung von Flachs mit einem hohen Anteil an zellulosehaltigen Nesselfasern. Zudem wurde der Einfluss unterschiedlicher Flammschutzmittel untersucht, wie z.B. anorganische Hydrate, Halogene und halogenfreie Dämmschichtbildner, wobei Synergisten (Antimontrioxid und Nanotonerden) mit 30 und 50 Gew.-% Flachs/PP-Compositen untersucht wurden. Außerdem wird die mögliche Optimierung des Aluminiumtrihydratgehalts Polypropylen/Flachs im Verbundwerkstoffen mit Bezug auf den Flammschutz (Flammhemmung) und die mechanischen Eigenschaften untersucht.

Als erstes muss als Grundlage für die Ergebnisse der vier Themen, die optimalen Behandlungsmethoden für die Faser und die Polymermaterix definiert werden. Flachsfasern, die durch Alkalinisation und Polypropylenmatrizen, die durch Maleinsäureanhydrid gepfropftes Polypropylen behandelt wurden, zeigen die besseren Eigenschaften gegenüber den anderen Möglichkeiten der Behandlung. Anschließend werden die optimalen Zusammensetzungen für geplanten Eigenschaften tabellarisch zusammengefasst.

Als zweiter Punkt lässt sich hinsichtlich des Extruders zusammenfassend sagen, dass die Multi-Prozess Elemente und Zahnelemente auf einen möglichen signifikanten positiven Einfluss auf die mechanische Eigenschaften des Faserverbundes hin überprüft werden. Die Fasergröße wird dann statistisch mittels einer Weibull-Verteilung Funktion dargestellt.

Im dritten Schritt soll es sich anhand der Ergebnisse beweisen lassen, dass Fasermorphologie, Werkzeugtemperatur, Schmelztemperatur und Einspritzdruck eine bedeutende Rolle auf die Qualität der mechanischen Eigenschaften und des Fließverhaltens des Verbundes haben. Ein empirisches Modell wurde für die Fasergehaltsverteilung etabliert.

Schließlich steht die Schlagzähigkeit in Vordergrund, welche durch den Einsatz von Brennesselfasern gegenüber Triacetin und EPDM deutlich verbessert wurde. Parallel dazu zeigte das Flammschutzmittel Ammoniumpolyphosphat die besten Ergebnisse, jedoch erreichte das mineralische Aluminiumtrihydrat nach der Optimierung zu 40 Gew.-% ein gleichhohes Flammschutzniveau.

Summary

This work aims to explore the possibility of producing thermoplastic polymer reinforced by natural fibres (case study: Polypropylene reinforced with flax) with optimised properties. The investigated properties are the quality level of coupling between the fibre and the polymer matrix, mechanical properties, consistent fibre content in case of injection moulding, low water absorption. The optimisation study is extended to include the effect of the functional additives like flame retardants and impact modifiers.

The thesis contains eight chapters. First chapter begins with a historical background about the applications of natural fibres, their decline accompanying the development of polymers and their revival in the last decade with the corresponding market statistics. The problems, associating the application of natural fibres, such as adaptability to compounding technology, thermal limitations, lack of material databases and lower properties compared with synthetic fibres composites are addressed. The chapter defines the working objectives of the whole work.

Second chapter is a review chapter. Firstly it lists the classification of natural fibres regarding type, morphology, size, composition and mechanical properties. A brief description is given about the Process hierarchy from plant harvesting to the production of different fibre forms prepared for compounding with polymer. The geometrical and mechanical methods for fibres are also reviewed. Second section in this chapter deals with the thermoplastics and the importance of polypropylene. Finally, natural fibre polymer composites are reviewed regarding the production techniques, the composites' mechanical properties and the effect of the functional additives.

Third chapter shows the study structure for optimisation separated into four parts (A- fibre matrix coupling, B- compounding process, C- Injection moulding parameters, D- Effect of additives). The chapter lists all the materials used in this work (natural fibres, thermoplastics, coupling agents, impact modifiers and flame retardants). The chapter summarises the compounding techniques, testing samples preparation and the related standards.

Fourth chapter presents the different fibre/matrix treatments for improved coupling and the quantity optimisation of the best treatment. Fibre treatment is done by alkalinisation alone or combined with trimethoxy vinylsylan or combined with acrylic acid. Polypropylene treatment is by trimethoxy vinylsylan or maleic anhydride grafted polypropylene or acrylic acid grafted polypropylene. The system of alkalinised fibre and matrix treated by maleic anhydride grafted polypropylene is found to be in general the best system regarding the mechanical and water absorption properties. The second part of the chapter deals statistically with optimising the amount of maleic anhydride grafted polypropylene with respect to the fibre content.

Fifth chapter deals with the compounding processes namely kneading and extrusion. More focus is given in this chapter for the extrusion because of its importance for industry. The effect of different extruders' layouts on the resulting composite mechanical properties is studied and correlated with the development of the fibre size

along the extrusion length. A Weibull function is suggested to describe the fibre length distribution and hence the shape and scale parameters are defined.

Sixth chapter deals with the optimisation of the injection moulding parameters. The effect of the injection moulding parameters (Temperature, injection pressure, mould temperature and screw speed) is studied regarding the mechanical properties. Mould temperature, measured temperature and injection pressure are found to be the significant factors influencing the mechanical properties of the injection moulded composite. Second part of the chapter studies the effect of the injection parameters on the flowability and fibre content consistency by a spiral mould. Fibre content variation can be controlled by the processing parameters (pressure and temperature). However a compromise is needed because the factors leading to consistent fibre content are contradicting with the requirements of high flowability. Effect of fibre stiffness and morphology (branched or not) is discussed. Fibres of non-branched with high flexural strength like cellulose show higher flowability and more homogeneity and consistency of fibre content in comparison to the branched low flexural strength fibres like hemp and flax. The last part of the chapter deals with the modelling of fibre content distribution along injection moulding one and two-dimensional parts using empirical formulae.

Seventh chapter deals firstly with the additives for increasing the impact strength of flax fibre thermoplastic composites. Three methods are tried namely plasticizer (Triacetin at 5, 10, 15 and 20 wt%), elastomeric rubber (Ethylene propylene diene monomer EPDM at 5 and 10 wt%) and hybridisation of flax with the high cellulosic content nettle fibre. The three methods deal with polypropylene reinforced with either 30 or 50% flax. Mechanical testing shows that nettle fibres induce better impact strength compared to flax. Therefore the addition of 10-15 wt% of nettle fibres instead of flax improves the impact strength with 11-16 wt%. The amount of the improvement amount depends on the initial flax loading. EPDM improves the impact strength with only 8% at flax loading of 50%. Triacetin represents the worse results especially with 50% flax. The second part of the chapter deals with flame retardants. A review is done for different flame retardants on different fibre types of NFTC. Flame resistance as well as the resulting mechanical properties are considered. Disregarding the results of decabromodiphenyl oxide DECA (because of the healthy regulations), ammonium polyphosphate has the best combination of flame retardance and strength. Synergetic effect of antimony tri oxide with DECA and nano clays with ammonium polyphosphate is also studied. Mineral flame retardants like magnesium hydroxide or aluminium trihydrate are tried because of their good ecological impact. Mineral flame retardant should be added in enormous percent to reach high flame retardance level. So a study is done to balance the mineral flame retardant with respect to the mechanical properties and flame retardance level. Eighth chapter lists the main outcomes of this study and finally states the challenges which are not solved yet and need to be further studied.

List of Symbols

Vf	Volume fraction	
σ	Fibre strength	[MPa]
$\sigma\phi$	Fibre strength	[MPa]
σ_{μ}	Matrix strength	[MPa]
σ_{χ}	Composite strength	[MPa]
η_{o}	Orientation factor	
η_{λ}	Length factor	
l_c	Critical fibre length	[mm]
d	Fibre diameter	[mm]
τ	Interfacial shear strength	[MPa]
E	E-modulus	[MPa]
E_c	E-modulus of composite	[MPa]
r_f	Fibre radius	[mm]
R	Inter-fibral distance	[mm]
E_f	Fibre elastic modulus	[MPa]
G_m	Matrix shear modulus	[MPa]
FC	Fibre content	
N	Screw speed	[rpm]
FC_{max}–FC_{min}	Variation in fibre content	
C_I	Interaction coefficient	
ψ	Fibre distribution function	
t	Time	[s]
ϕ	Fibre angle	
T	Temperature	[°C]
P	Pressure	[bar]
FL	Flow length	[cm]
r^2	Relative measure of fit	
L	Length of fibre	[mm]

List of Abbreviations

AA	Acrylic acid
ABS	Acrylonitrile-butadiene styrene
APP	Ammonium polyphosphate
AR	Aspect ratio
ATH	Aluminium trihydrate
DECA	Decabromodiphenyl oxide
DEFI	Fibre diameter (Dynamic image analysis)
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
E’	Storage modulus
E’’	Loss modulus
EPDM	Ethylene propylene diene monomer
FR	Flame retardant
GF	Glass fibre
HDT	Heat deflection temperature
LDPE	Low density polyethylene
LEFI	Fibre length (Dynamic image analysis)
MAPP	Maleic anhydride-grafted-polypropylene
MARHE	Maximum average rate of heat emitted calculated from HRR-Time per m²
MPE	Multi-Process-Elements
NaOH	Sodium hydroxide
NF	Natural fibres
NFC	Natural fibre composites
NFTC	natural fibre thermoplastic composites
NREL	Method of National Renewable Energy Laboratory for lignin content
PA	Nylons
PC	Polycarbonate
PCL	Polycaprolactone
PE	Polyethylene
PET	Polyesters
PHRR	Peak heat release rate
PLA	Poly lactic acid
PMMA	polymethyl methacrylate
POM	Polyacetal
PP	Polypropylene
PS	Polystyrene
PS	Polystyrene
PVC	Polyvinylchloride
RMSE	Absolute fit of the model to the data–Closeness
S/N	Signal-to-noise ratio
Tg	Transition glass temperature
THR	Total heat released per m²
TMVS	Trimethoxy Vinylsilane
TSR	Total smoke released normalised for the surface area of the specimen
TT-flame out	Time to flame distinguishing

TTI	Time to stable ignition of at least 5 s
TTPHRR	Time to peak heat release rate
UV	Ultra violet
WPC	Wood plastic composite
ZB	Zinc borate

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1 Introduction and problem definition

1.1 Introduction

Implementation of natural fibres as a reinforcing material is already known and evidenced in the history. Egyptians, 3000 B.C., used straw in combination with clay for building of house walls and the Chinese as well laminated wood with horn and sinew to develop their laminated composite bow. The use of natural fibres found new applications starting from the late 19th century in the machine age. For example, housing and lining of telephones and radios were made of composite by compounding ground wood in schellac [Lew07]. An inspiring idea arose at the thirties of the 20th century to use the natural fibres in dynamic loading applications like vehicle and aeroplanes. Henry Ford investigated a variety of natural materials like cabbages and cornstalks and in 1942 showed the first prototype car made from hemp fibres. Similarly, the fuselage of the twin-engine British aircraft DE Havilland DH – 88 Comet was made of phenolic resin reinforced with flax yarns. The aircraft was already used in the Second World War. Not lately in the fifties, the body of the East German Trabant car was constructed from phenolic resin reinforced with cotton fibres [Ble02].

However in 1938, the Owens-Corning Fibreglass Corporation is established. The corporation commercialised its breakthrough product namely the glass fibre [Loe75]. The glass fibre filaments are characterised with their consistent properties, thermal resistance and high mechanical properties. Consequently, the attention to natural fibre application is depleted and seems to be old-fashion. But less than 30 years later and at the early 70s, the scientific committee figured out the price of the energy needed in the production of the synthetic fibres as well as other petrochemical industries. This energy is mostly brought from coal, petroleum and natural gas fossil resources. Particularly, with the steadily increasing demand for the oil and the depletion of the finite sources of fossil oil, the oil price is getting higher which leads gradually to the infeasibility of the high energy consumption plants. Additionally, the drastic increase in the volume of wastes arouses the question of how we can recycle these products again. Finally, the increasing evolving CO_2 in the earth atmosphere, which in turn results in the global temperature increase, points out to the necessity to decrease the volume of the annual used fossil oil. Therefore the European community (EU) has issued a package of legislations with 20-20-20% targets at 2020 in comparison to 1990 levels; namely 20% reduction in the greenhouse emission, 20% increase in the application of energy by renewable resources and 20% improvement in the energy efficiency.

As a result of the above mentioned reasons, the focus shifts again gradually to the natural fibres which are characterised by their availability, low price, neutral carbon emission and low energy consumption needed for processing. Regarding the density, it is obvious that natural fibres of almost 1.3-1.5 g/cm^3 are superior to glass fibres of 2.54 g/cm^3. This saving in weight leads to saving in energy needed in transport vehicles [Bos04]. Regarding the mechanical properties, some fibres like flax, hemp, kenaf and sisal are characterised with tensile modulus and tensile strength which are comparable

to the 70 GPa of E-glass fibre [Ver12], [Hau81], [Her98], [Zie05]. Regarding the price, glass fibres are in the range of 0.7-1.4 €/kg which is relatively higher than that of natural fibres which lies in the range of 0.2-1.0€/kg depending on the natural fibre type, quantity and treatment [Jos04]. However; It is unlikely that this shift can be easily or quickly implemented in the market because of the natural fibres' drawbacks like dimension instability (4), lack of results' reproducibility [Gar08], [Tah06], low thermal resistance [Gar08] [Cle05], biodegradation with rotten smell and incompatibility with non-polar polymer matrices [Arb05]. Over and above, there is a big lack in concrete databases for the natural fibres [Arb05] or their composites regarding the thermal, physical and mechanical properties. Therefore, the application of natural fibres is limited to non-highly loaded products in civil, electronic appliances and automobile industries. Some examples of these applications are like the construction profiles in roofing, wall linings or in furniture and household substances in mobile phones bodies and covers and finally in the automobile industry. The application of natural fibre is focused mostly on the interiors of car doors, dashboards and rear shelves [Car13]. Application of natural fibres composites in the European countries reached up to 80000 tonnes in 2012. Wood plastic composites (WPC) still possess the highest share of 36% in comparison with the other fibre types as shown in Figure 1-1. This is logic as WPC has already established processing techniques especially the compression moulding and the extrusion method. Other fibres comprise of the remaining 64%. The share of using a certain natural fibre in natural fibre composites (NFC) production is not correlated with the world production of the fibres.

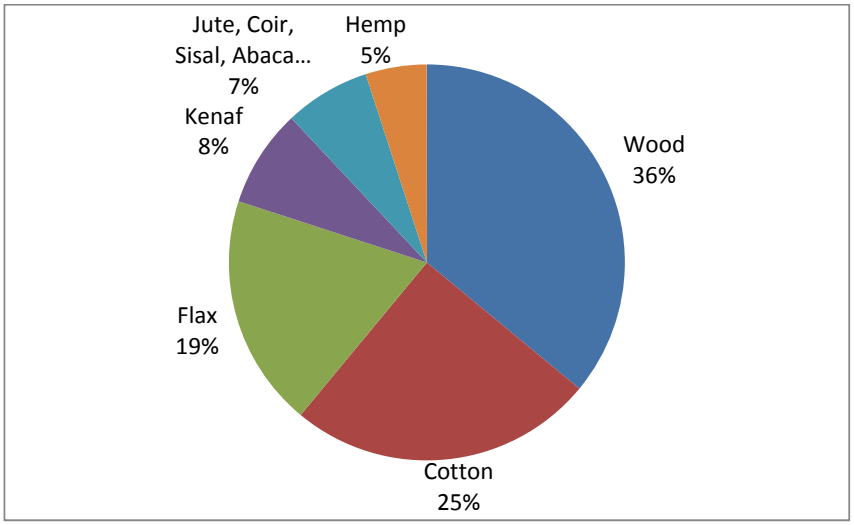


Figure 1-1: Use of natural fibres for composites in the European automotive industry 2012 [Car13] (14)

World consumptions of flax and hemp in 2011 are 750 and 85 kilo tonnes [Ver12] while their shares in NFC production are 19% and 5% respectively [Car13]. For comparison with the data from 2005, cotton will not be considered. Comparing the market shares of natural fibre annular consumption between 2005 and 2012, it is obvious that there is an increase from 19000 tonnes [Car06] to 30000 tonnes [Dam13] as shown in Table 1-1. Thus implies an increase of just 11000 tonnes over 7 years. This small increase depicts the effect of the problems facing this new engineering material. It is also

interesting to show the retreat of flax share and the jump of other fibres like kenaf and hemp. This is not attributed only to the increase in price as mentioned [Dam13], but actually due to other aspects like the growing conditions or the colour of the end-product.

Table 1-1: Natural fibres in European automobile industry in years 2005 and 2012 [Dam13]

Fibre use in year 2005	**Total: 19000 t**	**Fibre use in year 2012**	**Total: 30000 t**
Flax	64,1 %	Flax	50 %
Jute/Kenaf	11,2 %	Kenaf	20 %
Hemp	9,5 %	Hemp	12 %
Others (mainly coir and abaca)	7,9 %	Others (jute, coir, sisal, abaca)	18 %
Sisal	7,3 %		

1.2 Problem definition

The problem of getting higher shares in the market for NFC is not only a psychological barrier. NFC are not trusted like glass fibre composites [Bos04]. It should be admitted that there are also real problems which should be solved in advance to increase the NFC opportunity in the market. These problems are like:

- The technology of compounding fibres with the host polymer matrix is not well adapted and the corresponding process parameters are not well defined to attract the manufacturers. So, the manufacturer tried NFC injection moulding and just he got a burned product or clogging in the machine screw, he easily gave up because of the machine and man hour costs. That explains why the press moulding techniques for both thermoplastic and thermoset polymers represent 96%, as seen in Figure 1-2. Most of the NFC are produced by compression moulding. This is attributed to the already guaranteed techniques for compression to attain light weight product with acceptable crash behaviour and dimensional stability resisting to deformation. Compression moulding of NFC reduced recently the area weight to 1,500 g/m^2 (with thermoplastics) and 1,000 g/m^2 (with thermosets) which is much better than pure plastics or glass fibre composites [Car13]. The other processing techniques especially the shear rate processes like injection moulding and extrusion represent trivial share in the production techniques, even compared to the thermoplastic press moulding only. That is the reason of the study in this work to have better shearing compounding processes in order to attract more decision makers to count on NFC. The shear compounding technologies, like knead compounding, extrusion and injection moulding, deal mainly with thermoplastics as polymer and non-

woven fibres as reinforcements like fibre slivers, chopped fibres or compressed pellets..

- Incomplete or even empty databases about the physical, rheological, electrical and flame resistance behaviour of NFC products in comparison with already settled databases for glass fibre composites. Therefore, the automobile and of course the more cautious aircraft industry will not give the green light to such NFC components before they get sure about their behaviour under crash case, fire resistance, etc…
- Lack of standardised methods for testing the fibres' quality regarding the selection of the fibres' sample, the tensile test conditions like gauge and clamping lengths.
- Low impact strength, despite the promising tensile modulus or strength values, still represents a big drawback in NFC especially in case of chopped fibres reinforced composites.

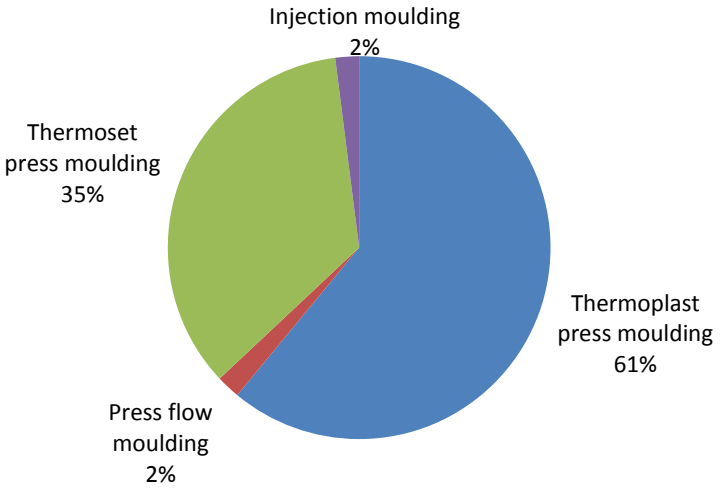


Figure 1-2: Use of natural fibres (19000 tonnes) in composite production for the German automotive industry 2005 [Car06]

The future of NFC depends on the interaction of different factors as follows:

- Price of the fibre which depends on its availability, extraction technique, reproducibility and certification. For example, the desired quality of fibres can be attained by retting which will result in higher production costs and higher ecological burden due to the increased demanded oxygen [Dam13]. The certification is also a major issue where the Asian market, which is the main supplier of natural fibres, is still away from being capable to supply consistent quality. Price is expected for fibres like sisal due to the limitation in production and the increase in need while other fibres like the regenerated celluloses are already high due to the processes required to extract the almost pure cellulose structure [Roe09].
- Increasing need to the bio-based polymers, such as Polyhydroxy Alkanoates (PHA) and Polylactic acid (PLA), will definitely increase the need to the

reinforcing natural fibres. It is expected that the production of bio-based polymers will be tripled from 3.5 million tonnes in 2011 to nearly 12 million tonnes by 2020 [Dam13].

- Characterising the effect of the required additives like plasticisers, ultra violet (UV) stabilisers, antioxidants, pigments, flame retardants, copolymers and formability additives.
- Filling the missing required testing standards for both the fibres and the products. For example, unification the tensile test of the technical fibre is necessary. From the product side; the non-destructive testing (NDT) for both online production and after-sale services.

1.3 Work objectives

This work aims to explore the possibility of producing thermoplastic polymer reinforced by natural fibres with improved properties. The planned compounding mechanism is the extrusion technique because it suits the needs of industrial scale production. However some trials are carried out by kneading for the sake of controlled composition. Polypropylene (PP) is selected as the default candidate thermoplastic for the investigations. PP still represents the main injection-moulded thermoplastic in Europe [Dam13] which is 92% of the 15000 tonnes of production volume with natural fibres.

The planned work will investigate the problem of fibre matrix coupling with the non-polar polymers like PP. Different treatments for both the fibre and the polymer matrix will be carried out. The best method of them, regarding physical properties like water absorption and mechanical properties, is selected for further investigations. Second part of the work discusses the different rules mentioned in literature about the selected coupling agent and then an optimisation experimental study is conducted to find the best one. In this part, different fibres are investigated like flax, hemp and jute.

After the definition of the fibre treatment, fibre-matrix coupling agent and the percentage required for better coupling between the fibre and the matrix; the compounding process, twin screw extruder, is investigated where different screw configurations are used and the effect of the screw configuration as well as the process parameters like speed and temperature profile on the mechanical properties of the extruded NFC. Additionally, the effects of the extruder configuration and the process parameters are studied in terms of the fibre morphology.

The final extruded materials are injected at different processing parameters to see their effects on the mechanical properties as well as the flowability of the NFC and the fibre distribution along a spiral injection mould. Hence, a model is constructed trying to explain the behaviour of fibre distribution.

The effect of required additives for enhanced properties is investigated. Impact modifier is an important topic as previously mentioned which needs a lot of work. Then finally the effect of flame retardants (FR) additives is discussed. This part contains a comprehensive study of different FR (Inorganic hydrates, halogenated, halogen-free intumescent, etc…). The results help in constructing a material selection chart combining the mechanical property with the required flame retardance level.

Figure 1-3 shows the concept of the thesis in the above mentioned four sectors (Blue blocks: coupling selection and optimisation, Red block: compounding process definition, Green blocks: injection moulding study with respect to the mechanical properties and the flowability besides to its modelling, Brown blocks: Effect of additives).The concept of planned work is not simply sequential as shown by the light blue arrows. It is expected to have feedback effects by the yellow arrows. However, it may be easier for this study to study the sequential blocks as appears in Figure 1-3.

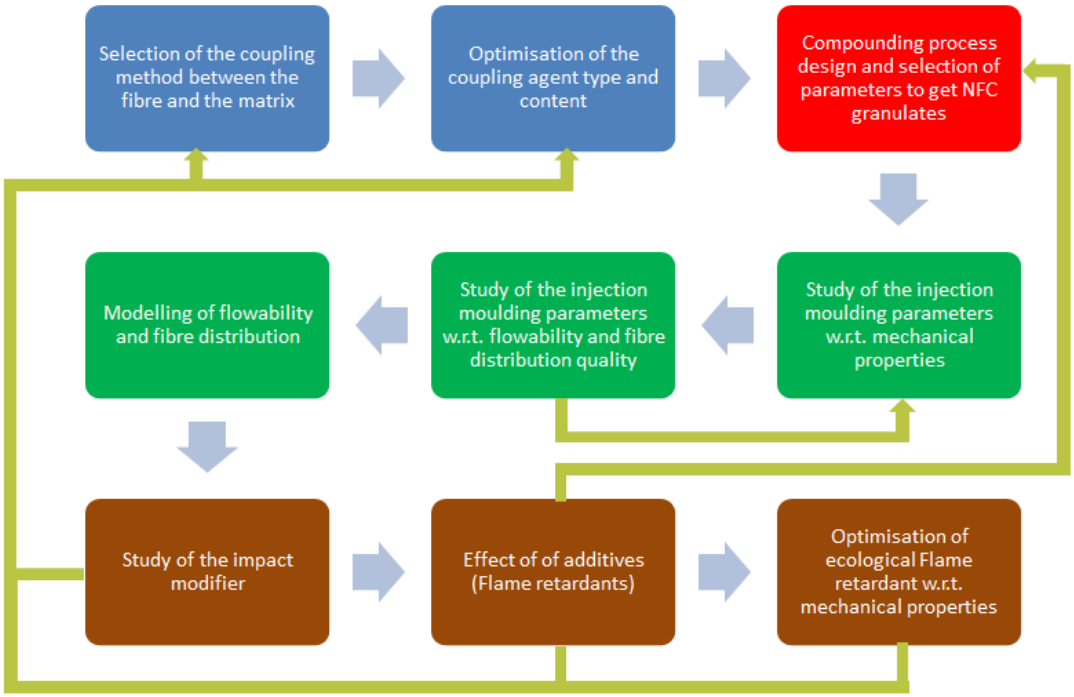


Figure 1-3: Concept of the thesis in this study

2 State of the art

2.1. Natural fibres

The term “fibre” stands for a class of hair-like materials that are continuous filaments or are in discrete elongated pieces, similar to pieces of thread, such that their length to width ratio exceeds 10 [Tah07a].

The term “Natural fibre” is ambiguous in texting or at least too general if not defined or limited to one type of the natural fibres. That is because natural fibres are mainly classified to plant (cellulosic) fibres, animal (protein) fibres and mineral fibres [Moh01], [Joh08]. Plant fibres are like flax, hemp, kenaf, grass, etc. while animal fibres are like wool, silk and feather. Mineral fibres are like asbestos and actinolite. In this study, the term “Natural fibre” is limited to the plant cellulosic ones.

Better understanding of the behaviour of the plant fibres during shear processing, or even the explanation of fibre distribution and its effect on the mechanical properties of the final product, requires a survey of the plant fibre types. The following review considers only the intrinsic properties related to the flow behaviour such as the fibre constituents, dimensions and physical properties. Other intrinsic properties like odour and colour are considered in this work only qualitatively. This means that the samples, which show no burning aspects, are subjected further to mechanical or physical tests. Other factors, which depend on processing or transport problems, like the impurities level and the fibre neps in spite of their decisive effect on the final properties are not discussed herein.

2.1.1. Fibre types, morphology and size

Different classification systems are used for the plant fibres [Mue10a], [Mue12]. Plant fibres can be generally classified according to the old grouping method of the flowering plants which is the number of cotyledons in the seeds (cotyledon is an important part of the embryo enclosed in the plant seed). Monocotyledonous plants are plants having seeds with one cotyledon while the dicotyledonous seeds consist of two cotyledons. Monocotyledonous plants are like coir, sisal, banana and abaca. Dicotyledonous plants are such as the bast fibres of flax, hemp, jute, kenaf and nettle. This classification describes the most likely locations of extracting the technical fibres. The vascular band, from which the fibres are extracted, appear in a ring form of thick bundles or fibre clusters for the dicots, while in case of monocots they are not taking place only around the periphery of the ground tissue, see Figure 2-1 for different stems of monocots and dicots. The arrangement of the vascular bundles and hence the distribution or the shape of the fibres are depending on the plant part whether it is the stem or the root.

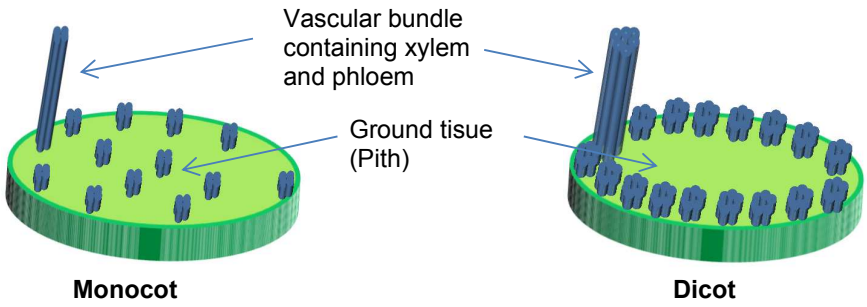


Figure 2-1: Position of fibres in mocotyledonous and dicotyledonous plants [Bio16]

Plant fibres are also classified according to the plant part from where the fibres are extracted namely:

- Seed (e.g. Cotton and Akon)
- Bast or Stem (e.g. Flax, Hemp, Jute, Kenaf, Nettle, soft and hard wood)
- Fruit and fruit hair (Coir, Kapok and Paina)
- Leaf sheath (Sisal, Abaca, Pineapple and Banana)
- Halm or grass (Bamboo, rice straw and wheat straw)

Muessig et al. [Mue12] classified the fibres according to their fineness in the order of coir, sisal, abaca, hemp, flax, ramie, cotton, micro cellulose from ultra-coarse to ultra-fine. Ability to spinning increases with the increase of fibre fineness. The morphology of the natural fibre is described qualitatively [Bio16] in regard to:

- The number of individual fibres per unit technical fibre,
- Degree of packing in the fibre cross section. For example, the lumen (the central void in the fibre surrounded with cell wall) in flax and hemp is smaller than that of coir,
- The fibre aspect ratio defined by Equation 2- 1,

$$AR = L / D_{eq}$$ Equation 2- 1

Where *'AR'* is the aspect ratio, *'L'* is the fibre length and 'D_{eq}' is the equivalent fibre diameter.

Alves et al. [Alv13] correlated the morphology of the fibre with the fibre mechanical property. Morphology effect is expressed in terms of the bearing area which is the fibre cross section as well as the number of individual fibres (cells) and the cell wall size as shown in Figure 2-2. The fibre composed of many fibre cells. Each unit cell composed of lumen in the middle surrounded by the cell wall (actually consists of three layers but the secondary one is the bulky). Cells unite with each other with the middle lamellae full of hemicellulose and lignin in case of wood or pectin in case of flax. The middle lamella substances represent the binding material between the individual fibre cells. It is concluded [Alv13] [Thy06] that Increasing the cell wall thickness of the cell and decreasing the lumen resulted in higher fibre strength and young's modulus as well. Another important aspect is the helix angle of the micro-fibril angle by which the micro-

fibre inclines to the bundle axis as shown in Figure 2-3. Each cell wall around the lumen grows in a spiral direction different from the next one. In general, this helix angle affects the fibre overall strength where smaller angle results in a higher stiffness and strength, while bigger angle results in a higher tensile strain [Mue12].

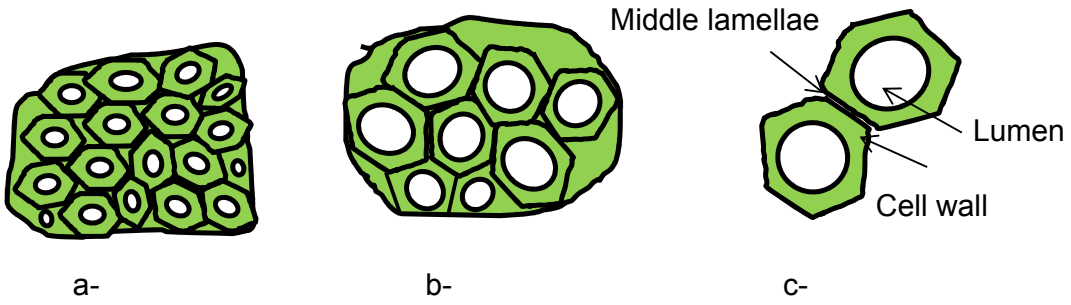


Figure 2-2: Schematic of Fibre cross section a- Small lumen b- big lumen c- Zoom in cell structure

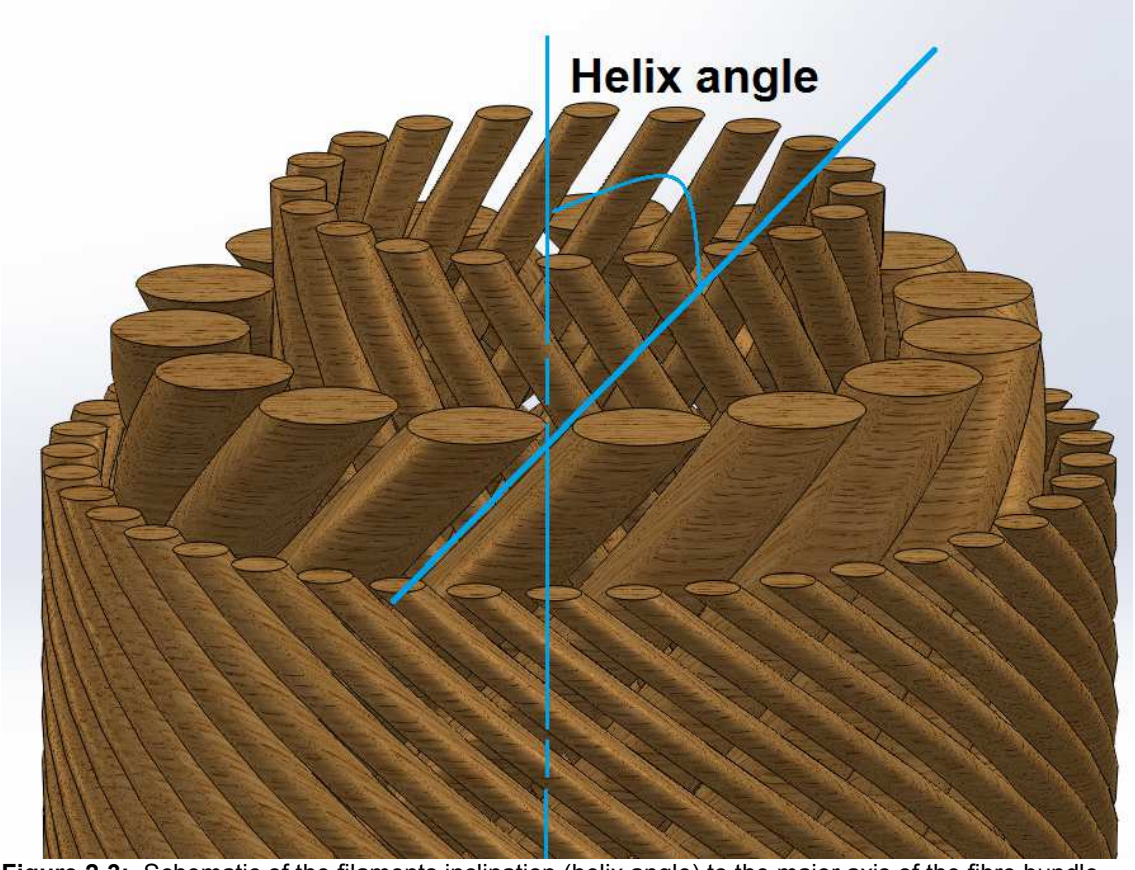


Figure 2-3: Schematic of the filaments inclination (helix angle) to the major axis of the fibre bundle

A wide scope comprehensive review of the dimensional and the mechanical properties for some cellulosic fibres is presented in [Mue12]. The problem arises in these reviews is that the dependence of the data on the manufacturing step from which the fibre is extracted and tested. That is attributed to the inaccurate or the ambiguous use of

natural fibre terminology. For instance; natural fibres can take the following forms namely technical, elementary, meso fibre, etc… [Bos02].

Figure 2-4 shows the classification of fibre in the structure of a flax stem. Bast fibre is the load bearing plant tissue. Technical fibre represents the commercial form of the supplied fibres to the industry of textiles or composite applications. After processing, the technical fibre is defibrilled to elementary fibres. This problem appears remarkably in the modelling of natural fibre composites where the applied data of the fibre mechanical strength and stiffness are normally taken out technical fibre testing. Technical fibre is actually a collection of smaller elementary fibres which are cemented with polymeric nature substances like hemicellulose, lignin, pectin and waxes. These substances have lower mechanical properties. In other words; the measured mechanical properties of the raw technical fibres are different from the actual properties after compounding (needed for modelling) [Gla99], [Gar00], [And06], [Tah08], [El-09b], [El-09c].

Table 2- 1 presents the reported diameter and length of some natural fibre. The status of the fibres is also mentioned whether the fibre is original (before processing) or extracted (after processing). The variation in the reported sizes is not only due to the status of the fibre regarding the received process, but also it depends on the harvesting time and the planting source. This variation is also attributed to the used method for measurement. For example, fibre length can be measured mechanically by tweezers or Almeter, or by image analysis systems using Fibre-shape scanning system [Mue10a] or by the dynamic image analysis QICPIC [El-14c], or even by using normal microscopy [Tah07a]. Another reason for this reported variation in measurement even using the same equipment is the different statistical evaluation method. For example, evaluation of fibre length can be based on the fibre number Q0(x), length Q1(x), area Q2(x) and mass Q3(x), decides significantly the final results [ISO04].

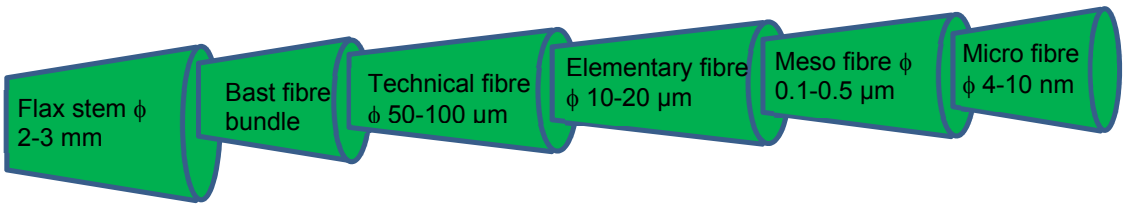


Figure 2-4: Terminology of a flax fibre according to the fibre extraction level. Data quoted from [Bos02]

The effect of hot shearing processes on fibre decohesion, defibrillation and fragmentation appears in the lower values of the extracted fibres denoted by superscript “e” in comparison with those of the original supplied fibres denoted by superscript “o” [Bea13], [Liu07], [Aus13]. Fibre decohesion means fibre individualization to fibres with smaller cross section whereas fibre fragmentation means fibre breakage to shorter lengths.

Table 2- 1. Dimensions of selected cellulosic fibres

Fibre	Flax	Hemp	Sisal	Kenaf	Wood fibre	Wheat straw*	Regen. celluloses
Diameter [μm]	21-35 [Zie05]o 1.7-76 [Mue10a] 10-25[Nil06] e 5.2-24.8*e	40-69[Zie05]o 3-51[Mue10a] 18-26[Nil06] e 5-34*e	99-166[Zie05]o 4-47[Mue10a] 18.5-256*o	12-50[Mue10a] 22.1[Ver04]e 72.6*o	25-35[Mue10a] 75-210*e	13-23 [Mue10a]	16-120*o 4.5-71.4*e
Length [mm]	79[Zie05]o 4-140[Mue10a] 3-50[Nil06]e 0.076-1.08*e	40-69[Zie05]o 3-51[Mue10a] 18-26[Nil06]e 5-34*e	278[Gar00]o 0.5-8[Mue10a] 0.17-2.4*e	1.5-11 [Gar00] 1.29[Ver04]e 3.59*o	1.2-3.6[Mue10a] 0.08-0.21*e	1.6[Mue10a] 0.36-0.56*e	As required

*Internal investigation. The values are out of the cumulative frequency distribution in 10% - 90% range of the measured size

o Original technical fibre

e Elementary fibre or extracted fibre after being processed

2.1.2. Fibre processing for NFC industry

Production of natural fibre, which is suitable for compounding with other polymers, is a long chain process. It does not start with fibre retting, but a long time earlier from the planting phase. The ratio of core to bast fibre, fibre length and components' contents are depending on the growing age [Row99]. For instance, the fibre length increased with time in the early part of the growing cycle then decreased and finally increased again by maturation. Lignin also increases as the plant age increases. Postponing the harvesting after the end of the flowering results in a higher percentage of lignified fibres [Ama10]. The annual fibres pass by five stages in their lifecycle in one season namely germination, growth, flowering, seed formation, and death or pulling.

Pulled plants are then usually retted. Bast fibres are retted to undergo a microbiological process where the fibres are loosened (pectins, hemicelluloses and lignin) and the bast fibre bundles separated from the non-fibrous core [Aki10]. The traditional methods applied to extract the long bast fibres are dew and water retting. Water retting is characterised by the saving in the field areas and the production of cleaner fibres, less contaminants, and lighter colour. Both methods require two to four weeks [Par11] to complete the retting process. Otherwise, under-retting situation will occur and fragments of cuticularised epidermis will remain on the fibre bundles [Mor99]. On the other side, over-retting leads to degrade cellulose and in turn the fibre size as well as the strength is reduced. There are also other methods of retting like mechanical retting, chemical retting and enzymatic retting. These methods are time saving in comparison to the dew and water retting methods. However they are not popular like them because of technological and safety measures needed. The Mechanical retting depends on the

hammering of fibres (e.g. kenaf) by a hammer mill or a decorticator and hence lot of short fibres are produced. This method is characterised with the low cost and the low fibre quality. Chemical retting depends on boiling the fibres in solutions of sodium hydroxide or sodium benzoate or hydrogen peroxide for 75 minutes. Over-retting in the applied chemicals leads to reduced strength and unfavourable fibre colour [Par11]. Enzymatic retting depends on good controlling of the conditions in the enzyme reaction (e.g. pectinase and xylanases) [Par11].
Fibres after retting and drying loose almost 40% of the original plants. Then, mechanical processes are applied to extract the fibres suitable for compounding with the polymers. Firstly; the fibres are cleaned from the shives (the non-fibrous core of the plants) and the cuticularised epidermis (a result of under-retting where pectines and hemicelluloses are not totally dissolved. This mechanical cleaning process is called scutching. The fibre bales are opened and thrown in a machine equipped with helical rollers. The scutching blades stroke the fibres to separate the shives which are then sorted out together with the short fibre bundles of less than 30 cm (tows) as defined by [Bos04], while the long fibres continue to be exposed to successive mill beating. The scutching mills are normally equipped with mills to align the fibres before being hammered in order to keep the fibre bundle orientation which in turn improve the mechanical efficiency of the coming-out fibres [Aki10]. Different outputs are coming out of the scutching mills namely:

- The long oriented fibre bundles which can be further hackled or combed. The long fibres represent 20% of the scutched fibres [Bos04] Naturally this percent depends on the fibre type and the scutching parameters.
- Tows and short fibres which can be screened for further processes or prepared for compounding with thermoplastic polymers. Tows and short fibres are only 12% [Bos04],
- Shives which can be used in artificial wood industries or blended with suitable lime binders in building material (e.g. MgO-cement) [Pre13], [Kid11]. Shives represent 67%[Bos04].

Next to scutching is the hackling or combing process where the fibres are combed to disentangle agglomerating positions in the scotched fibre bundles. Hackled fibres represent 70% of the original long fibre bundles after scutching. From this step, some short fibres and tows may result from the tanglement sites. Besides, the remaining contaminants are also removed. Keeping the integrity of long fibres results in producing long strands. These strands are called slivers (continuous fibre bundle) or rovings (slivers with smaller cross section and slight twisting). Out of this material, yarns are produced using wet spinning system. Bobbins of fibre yarns are used afterwards in weaving processes for fabrics and textile production. Twisting of sliver or yarn should not be understood interchangeably with the helix angle of the microfibril angle shown in Figure 2-3 because the microfibril angle grows naturally without induced stress while the twist angle affects the whole fibre bundle strength negatively [Bae12].

Figure 2-5 illustrates the sequence of processing carried out on fibres (specially the bast fibres) from the harvesting phase to the end-products short fibres, felts, slivers, spinned yarns, and woven fabrics. These end-products can be considered as possible

fibre reinforcing candidates for polymers to produce NFC. The motivation of this work is previously mentioned to be the increase of the share of NFC with shear compounding processes like extrusion and injection moulding. Therefore, the woven fabrics and non-woven felts will be disregarded in the study.

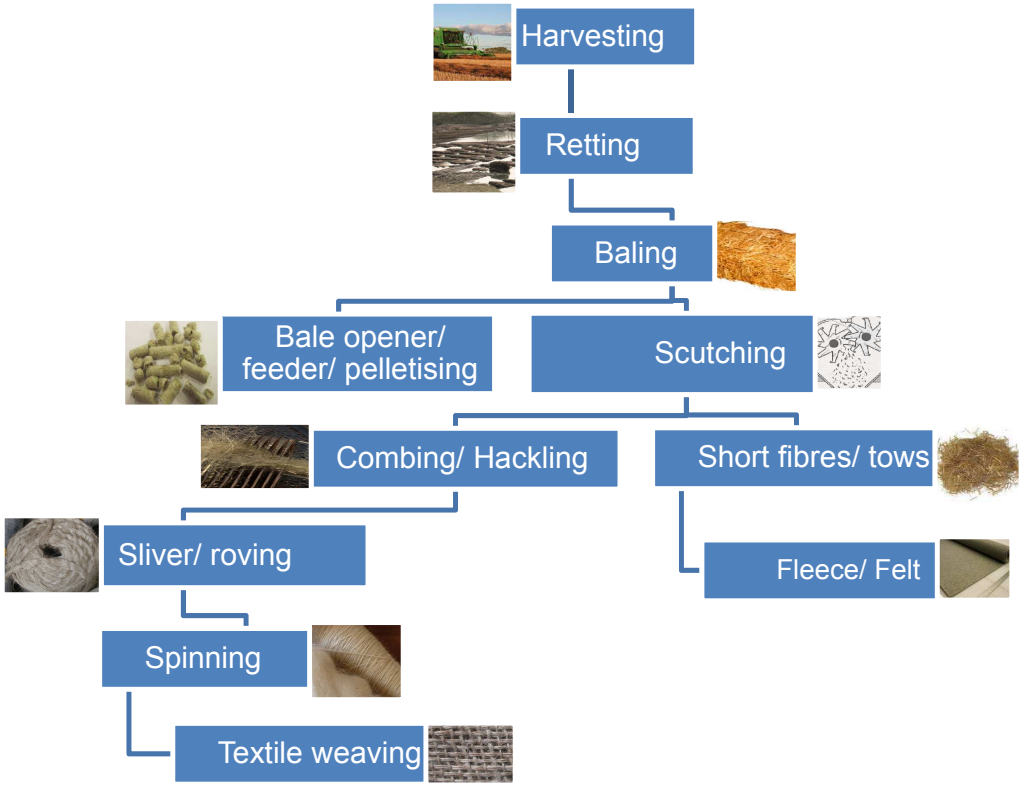


Figure 2-5: Process hierarchy from plant harvesting to the production of different fibre forms possible for compounding with polymer.

2.1.3. Fibre composition

As mentioned in 2.1.1, natural fibres are present in cell walls. They compose mainly of cellulose, hemicellulose, lignin, pectin, waxes, ashes and some other water soluble substances. The highly stiff component is the cellulose which comprises of almost 135 GPa in the axial direction [Sak62]. Ordered structures of cellulose are located in the plant cells especially the secondary cell wall. Cellulose fibres are embedded in an amorphous matrix composed of hemicellulose, pectin, proteins and lipids. Lignin fills the spaces in the secondary cell wall between the fibres and the amorphous matrix. The typical structure of the cellulose fibre is $(C_6H_{10}O_5)_n$ as shown in Figure 2-6. As obvious, cellulose wall is rich with the polar hydroxyl groups which cause the hydrophilic nature for the natural fibres.

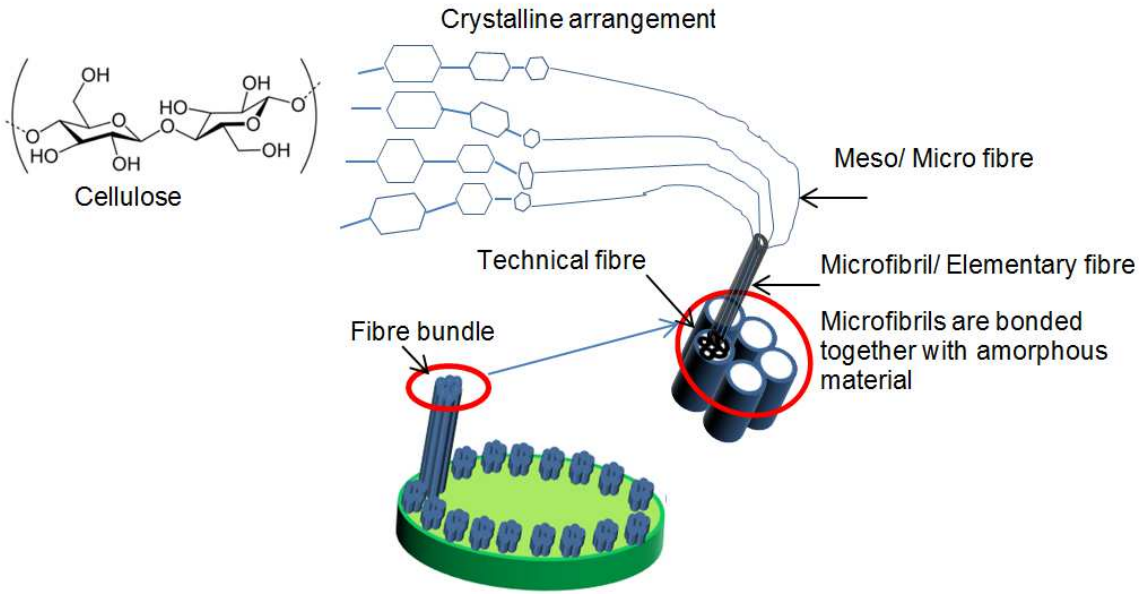


Figure 2-6: Schematic of the fibre structure from the plant stem to the cellulose molecule

Table 2- 2 lists the composition of the mostly used natural fibres (flax, hemp, sisal ...) from different sources in literature. All the literature lists the composition of cellulose, hemicellulose, lignin and pectin but other residues are sometimes neglected or collected together in one term like extractives which contains ashes and water soluble substances. Cotton is rich with cellulose then flax, hemp, sisal, jute, abaca and coir comes with the least cellulose content.

Table 2- 2. Composition of some selected natural fibres

Substance [wt.-%]*	Flax	Hemp	Sisal	Coir	Jute	Abaca	Cotton
Cellulose	70 71.2 71	70 78.3 57-77	66 73.1 47-78	40 35.6 --	65 71.5 45-71.5	60 70.2 56-63	90 -- --
Hemicellulose	17 18.5 18.6-20.6	16 5.4 14-22.4	12 13.3 10-24	0.2 15.4 --	15 13.3 13.6-21	21 21.7 15-17	4 -- --
Lignin	2.5 2.2 2.2	6 2.9 3.7-13	10 11 7-11	43 32.7 --	10 13.1 12-26	10 5.6 7-9	0.7 -- --
Pectin	2 2 2.3	1 2.5 0.9	2 0.9 10	3 5.1 --	1.5 0.2 0.2	0.8 0.6 --	4 -- --
Waxes/ Fats	1.5 1.6 --	0.7 -- --	1 0.3 --	-- -- --	0.5 0.6 --	1.4 0.2 --	0.6 -- --

Ashes	1.5 -- --	1.5 -- 0.8	0.3 -- 0.6-1	-- -- --	0.4 -- 0.5-2	-- -- 3	1.4 -- --
Water solubles/ Extractives	6 4.3 --	1 -- --	3.5 1.3 --	4.5 -- --	1 1.2 --	1.4 1.6 --	0.7 -- --

* The first row gets the data from Muessig [Mue10a], the second row from Van Dam [Van02] and the third one from Li [Li07], collected from [Moh01] [Row97].

Table 2- 2 shows that some measurements are close to each other, regardless the literature source. Other measurements are not identical such as lignin in hemp, cellulose in sisal and hemicellulose in coir. The variation in the measurements of the natural fibre composition can be partially attributed to the different methods in characterising the natural fibre constituents such as:

- Gravimetric wet chemistry techniques like Van Soest method [van67] and Updegraff method [Upd69]. The samples are ground almost to 40 mesh fineness and then repeatedly extracted using hot solvent mixtures and to separate pectines, hemicelluloses and celluloses after drying,
- Gas chromatography [Kac09]. It starts also with sample grinding, fining, hydrolysing and drying before it is exposed to gas chromatography. This method is coupled with mass spectrometry features for accuracy [Mic14],
- Near infrared spectroscopy concept is to measure the different intensities of the different waves transmitted or reflected through the fibre constituents of different structures. This technique is characterised with its simplicity in sample preparation, rapid results, non-destructive and good reproducibility [Par07],
- Laboratory analytical protocol (LAP) [Nre08], [Ham08] is recently wide spread. This technique uses a two-step acid hydrolysis to separate the biomass into quantitative forms. For instance; the polymeric carbohydrates (celluloses and hemicelluloses) are hydrolysed into the monomeric forms, which are soluble in the hydrolysis liquid. They are then measured by high performance liquid chromatography. The lignin is also separated into acid insoluble material and acid soluble material. The acid insoluble material may include ash and protein, which must be accounted for during gravimetric analysis. The acid soluble lignin is measured by ultraviolet visible spectroscopy. Protein may also partition into the liquid fraction.

The disadvantage of gravimetric wet methods is that it provides analysis of a single element (cellulose, lignin…) at a time. Gas chromatography drawback is that it is a time consuming technique to have volatile molecules out of small quantities. The near infrared method requires a wet chemical analysis for the sake of calibration before it can be applied. It needs also regular instrument standardisation and constant quality control. Spectrophotometry method suffers the insolubility of biomasses in most

commonly used solvents and even if solved there is a lack for appropriate calibration standards for the monomers incorporated in the lignin [Kli10]. LAP method is relatively accurate, because spectrophotometry is applied after the hydrolysis of polysaccharides, but there are laboratory safety concerns and too much steps required which can lead to experimental errors.

However what is actually the role of each constituent of the fibre? Cellulose, as mentioned previously, is responsible for the load transfer in the fibre. Cellulose is resistant to hydrolysis, strong alkalis and oxidizing agents but to some extent, is degradable when exposed to chemical and solution treatment. Hemicelluloses act like cement cellulose microfibrils. It is hydrophilic like cellulose but it is characterised that it can be easily hydrolysed by dilute acids and bases [Azw13].

Lignin (three-dimensional amorphous aromatic polymer) acts together with hemicellulose in binding the cellulose fibrils together. It is referred to as the plant cell wall adhesive [Ble02]. However it imparts rigidity to the plant. However delignification process allows more abundant hydroxyl groups on cellulose which are ready to react and thus higher moduli of elasticity and ruptures are attained [Che14]. Oppositely to hemicelluloses, lignin is hydrophobic. It resists acid hydrolysis and most microorganisms, show solubility by applying hot alkali. Lignin is also readily oxidised, and easily condensable with phenol. Lignin starts to decompose normally at earlier temperatures (i.e. 160°C for flax) [Cha10a]. This is attributed to the decomposition of relatively weak bonds [Koz08]. Therefore, higher amount of lignin lowers fibre decomposition temperature. However, lignin continues its thermal decomposition at a temperature range greater than those of hemicellulose and cellulose by the cleavage of bonds in the lignin aromatic rings. Lignin also releases less volatiles during decomposition. According to Manfredi et al [Man06], lower content of lignin is desirable to delay the ignition start time. However the aromatic rings present in lignin resist fibre oxidation. Cellulose also is considered as flammability cause because it produces the volatile flammables ‘Levoglucosan’ [Koz08] [Bas77], which consequently yield flammable and non-flammable volatiles and gases, tar, and char.

Pectin is a collective name for heteropolysaccarides and gives plants flexibility. Waxes consist of different types of alcohols [Joh08], [Sum10], [Azw13]. Wax and fats/ oils are substances on fibre surface substances which used to protect fibre [Won10] but actually after fibre treatment, most of the waxes, ashes and, pectines some hemicelluloses and lignin are removed.

2.1.4. Mechanical and physical properties

Table 2- 3 presents the mechanical properties measured for single fibres according to different literature sources. Bast fibres like flax and kenaf have relatively higher mechanical properties. Regenerated celluloses and Wood fibres also lie in the same category but with relatively low values, regarding the mechanical properties. Hemp, abaca and jute come next with less tensile strength and a great variation in the young’s modulus. Sisal, the leaf fibre, and cotton have then less tensile strengths and moduli. Finally, wheat straw (by-product halm fibre) and coir (the fruit fibre) lie apparently in

the lowest rank of the tensile properties. However coir has a high elongation value before break.

Of course, all the tensile results are dependent on the test parameters such as fibre size and test speed because they affect the development of the dislocation propagation and hence the fibre failure. But the most affecting point is the fibre length where longer fibre corresponds to more kink bands. Thus higher density of failure possible sites is found [Nil06], as illustrated in the scanning electron microscope SEM photo in Figure 2-7. This interprets the great variation in the reported measurements. However, a trend can be depicted from their values.

In comparison with the E-glass fibres (70 GPa Young's modulus, 2000-3500 MPa tensile strength, 2.5% elongation) [Eic01], it can be inferred that flax and kenaf have close results regarding the Young's modulus and elongation. However, the strength is utmost one half of the corresponding E-glass value. On the other side, the density of natural fibre ranges from 1.25 to 1.51 g/cm3 which is almost 40-50% less than glass fibre density (2.51 g/cm^3) [Bro00]. This difference in tensile strength between the natural fibre and the glass fibre should be considered when NFC performance (tensile, stiffness, impact strength…) is afterwards assessed.

Table 2- 3. Mechanical specifications of selected cellulosic fibres

Fibre	Young's modulus [GPa]	Strength [MPa]	Elongation at break [%]
Flax	27.6[Eic01] 27.6[Geo01] 8-100[Mue10b]	345-1035[Eic01] 78[Geo01]0 343-1500[Mue10b]	2-4[Eic01] 2-4[Geo01] 1.2-4[Mue10b]
Hemp	3-90 8.6-9.5[Sha13]	310-1110 690[Eic01] 244-277[Sha13]	1.3-6 1.6[Eic01] 2.3[Sha13]
Sisal	9.4-22[Eic01] 9-2[Geo01]2 9-38[Mue10b]	511-640[Eic01] 568-640[Geo01] 80-855[Mue10b]	2-7[Eic01] 3-7[Geo01] 1.9-14[Mue10b]
Kenaf	22-128[Mue10b] 23.6[Shi11] 17.9[Mir07]	180-1191[Mue10b] 1051[Shi11]	1.6-6.9[Mue10b] 4.5[Shi11]
Wood fibre	40[Mue10b] 17-28[Zha13] 13.5[Shi11]	1000[Mue10b] 400-1000[Zha13]	2.5-4[Zha13]
Wheat straw	5.7-6.39[O'D95]	23.4-31.2[O'D95]	---

Regen. celluloses	19.5-30.5[Adu06]	478-790[Adu06]	7.1-10.3[Adu06] 3.2-24.3[Roe09]
Coir	2.8-6[Mue10b] 4-6[Eic01]	95-270[Mue10b] 175[Eic01]	15-51.4[Mue10b] 30[Eic01]
Jute	3-64[Mue10b] 26.5[Eic01] 18[Geo01]	187-800[Mue10b] 393-773[Eic01] 226[Geo01]	0.2-3.1[Mue10b] 1.5-1.8[Eic01] 1.3[Geo01]
Abaca	12-72[Mue10b]	12-980[Mue10b]	1-12[Mue10b]
Cotton	5.5-12.6[Eic01]	287-597 [Eic01]	7-8[Eic01]

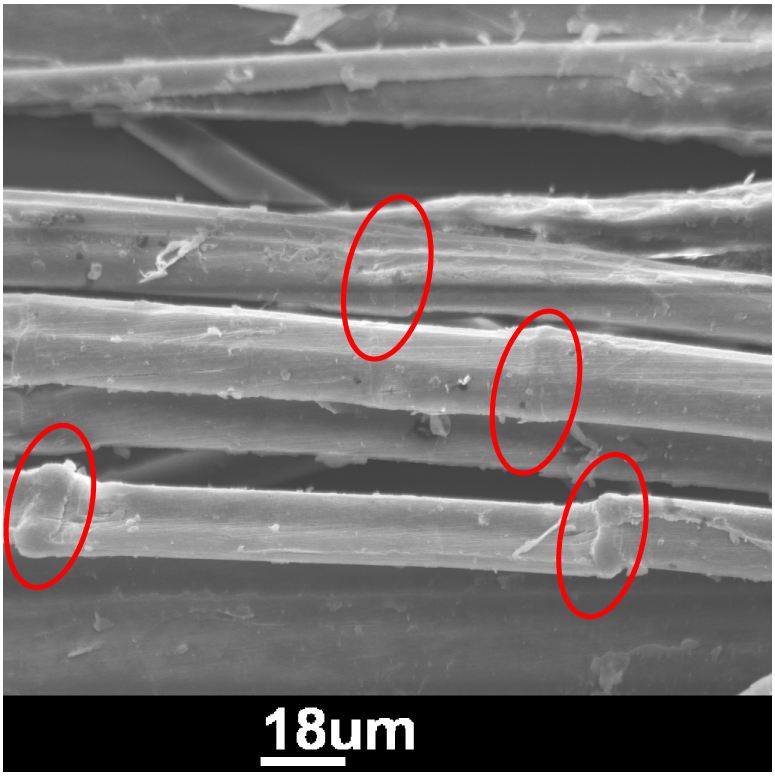


Figure 2-7: SEM picture of flax fibre with Kink bands

Another important point in the comparison of the natural fibres with respect to the synthetic glass fibres is the physical behaviour. For example and unlike glass fibres; natural fibres suffer from the problem of water absorption which leads to swelling or dimensional instability in the fibre transverse direction, biological degradation, unaccepted smell and change in mechanical properties [Sah99], [Dha07]. Drop in mechanical properties driven by water absorption is due to the fibre/matrix debonding,

fibre thinning because of the fibre soluble leaches and the induced micro cracks within the matrix because of the pressure drop [Azw13], as seen in Figure 2-8. Water absorption follows normally Fickian diffusion curve [Dha07] . It is in average between 6 and 16% at 65% relative humidity and 20°C. To suppress the water absorption by fibres, different approaches can be applied [Fao13].

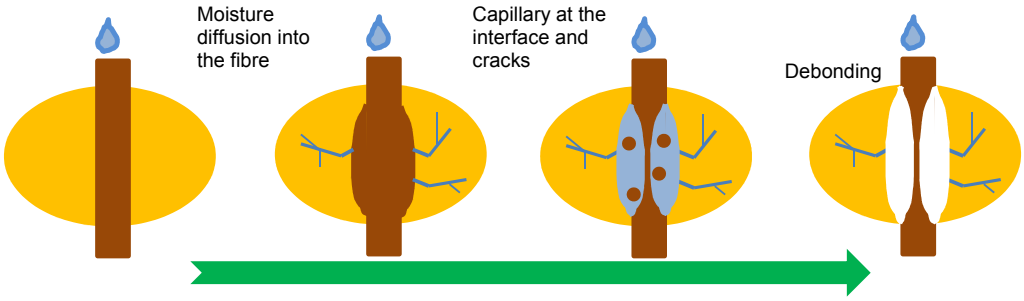


Figure 2-8: Water absorption effect on fibre matrix interface- adapted from [Azw13]

2.1.5. Characterisation tests

As shown in Figure 2-7, neither the fibre cross section nor its length is consistent. Also as mentioned previously, natural fibres suffer from the water absorption that leads to a change in the dimensions of the cross section. Other problems are also mentioned like the kink bands and the dependence of the characterisation test results on the parameters used. In other words, there is a need for standardisation of test procedures before using these data in further modelling. As reported in [Mue12], testing of fibres is defined to be after conditioning at 20°C/65% R.H. for 24 hours as described in DIN EN ISO 139. The issue of characterisation tests handles mainly the fibre size (length / fineness) and fibre strength.

Fibre length, as reported in 2.1.1 can be measured mechanically by Tweezer [Mue10a], microscopically or by the dynamic image analysis. Strength represents a bigger controversial problem. There are different concepts for measuring the strength of these irregular fibres. Taha [Tah07a] and Smole [Gru13] reported that they follow the single fibre concept. This implies fibre measurement and the application of tensile test on a lot of fibres. This method is standardised for fibres in ISO 5079/1995, IDIN 53816 and JIS-L1015 as shown in Figure 2-9, [Sch16]. Another way in determining the fibre strength is the collective tensile test where a bundle of fibres is loaded by a tensile load together. Obviously the collective strength is lower than the single element strength because the strength here is influenced by the single fibre strength distribution. However fewer tests are needed to reach a reliable result. Another disadvantage of this method is that the strength in cN/tex cannot be converted to MPa units. Some standards are already issued for flax characterisation like the French ANFOR standard XP T25-501 but it is still limited to flax fibres [Mue12] . Other standards are also developed by ASTM for flax colouration and cleanliness.

The increasing demand of natural fibre applications need in parallel adequate testing methods not only for flax and not limited by mechanical properties but also for fibre density, odour, colouration, purity and even grading for fibre structural problems like the linear density of the kink bands. Fibre density term is still confusing because it is normally to have the bulk density in the datasheet which is important by selecting extrusion feeder element. On the other side by final composite density and strength, the apparent density (real fibre volume without cavities and lumens) is the meaningful data. Therefore, attention should be given by using the proper terminology. The great variation of the results out of natural fibre testing requires also clear definition of the sampling procedure and the statistical parameters concerning the required confidence level.

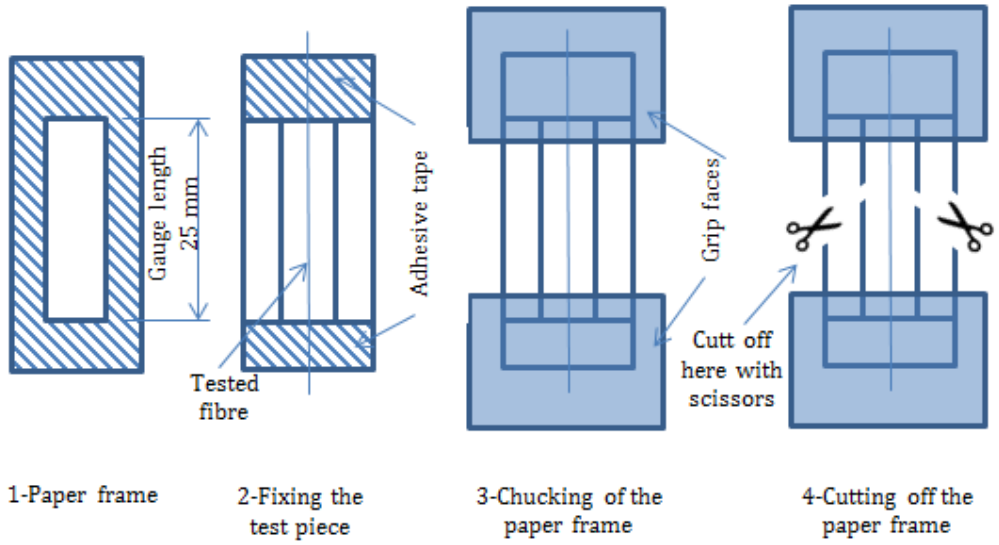


Figure 2-9: Single fibre test procedure according to [Sch16]

2.2. Thermoplastics and their composites

Thermoplastics are characterised by their melting and mouldability characteristics above a specific temperature and solidification under cooling conditions. Thermoplastics are very large linear molecules made of monomers (repeating units) linked together with covalent bonds along the molecular chains without cross linking [Bal12]. Thermoplastics are either amorphous or semi-crystalline. Amorphous thermoplastics (i.e. Polycarbonate (PC), Polystyrene (PS), acrylics (PMMA), acrylonitrile-butadiene styrene (ABS), polyvinylchloride (PVC)) are characterised by transparency, high impact strength and high heat deflection temperature (HDT), but they lack flexibility and resistance to chemical attack or stress cracking in comparison with the semi-crystalline thermoplastics (i.e. Polyamides (PA), polyacetal (POM), polypropylene (PP), polyethylene (PE) and the thermoplastic polyesters (PET)).

Application of thermoplastic reinforced with reinforcement fibres is widespread in automobile and E&E industries. Therefore it is necessary to understand the structure

of the mainly used candidate thermoplastics with natural fibres. According to [Dam13], 92 % of the polymers used in injected NFTC was polypropylene, while biopolymer matrix amounted to 6 % and only 2 % consisted of polyethylene. That is why the study will focus mainly on polyproyplene.

2.2.1. Polymer structure of PP

As mentioned in 2.2, the mechanical behaviour of the thermoplastic material depends strongly on the thermoplastic classification with respect to the temperature. Polypropylene is a linear semi-crystalline polymer. It is used in a wide variety of applications (i.e. food packaging, textiles, common plastic parts, laboratory equipment and automotive components). Its low density of 0.9 g/cm^3 and its well processing properties have made it to be a very common thermoplastic.

At room temperature and pressure the monomer propylene (C_3H_6), as illustrated in Figure 2-10, is a hydrocarbon gas, which is a by-product of petrochemical refining and of ethylene production by steam [Tah07a]. Polymerisation takes place by addition where the CH3 methyl group takes up space and constrains backbone bending on one space, herewith isotactic PP can be formed which in turn increases the mechanical properties. The most important characteristics of PP are its low processing temperature of about 165 °C or higher, light density, applicable resistance against chemicals like benzene, oils, acids, bases etc., relatively high mechanical properties like both tensile strength and modulus and its high scratch resistance [Lam01].

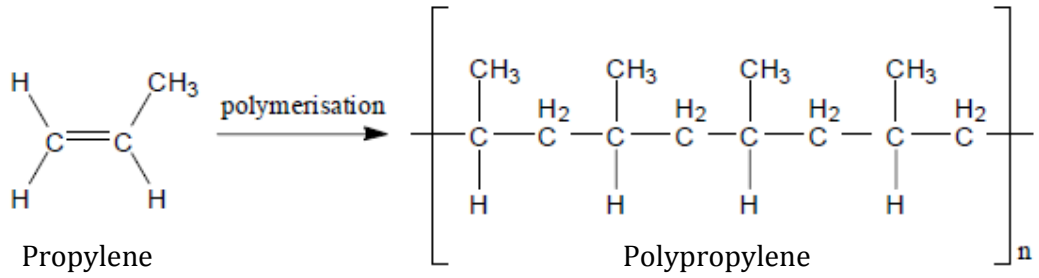


Figure 2-10: Chemical structure of polypropylene

2.2.2. Role of thermoplastic matrix in composite

Thermoplastic fibre composites consist of the thermoplastic matrix, the fibres and the interface between matrix and fibre. The interface serves in transferring the load between the fibre and the matrix [Bal12]. The role of the thermoplastic matrix is to distribute the load within the fibres evenly as much as possible. This requires in accordance to the presence of a good adhesion between the fibre and the matrix. Otherwise, the load transfer fails to happen.

Fibre volume fraction as well as orientation with respect to the loading direction plays an important role in the composite strengthening. The modes of composite failure are illustrated in Figure 2-11. Of course, the failure modes can be combined in more than one form.

a- Pull-out feature takes place at the interface when the fibre is aligned with the loading direction. Most likely the reason is either improper adhesion or weak bonding,

b- Fibre failure feature takes place firstly in the weak fibres or when the applied stress is unevenly distributed [Bos04] [And06],

c- Matrix failure occurs most likely in case of exceeding the local stress concentration more than the matrix maximum allowable stress. It can also take place when the load is in transverse direction to the fibres [El-09c],

d- Debonding takes place at the interface when the tensile loading is transverse to the fibre direction.

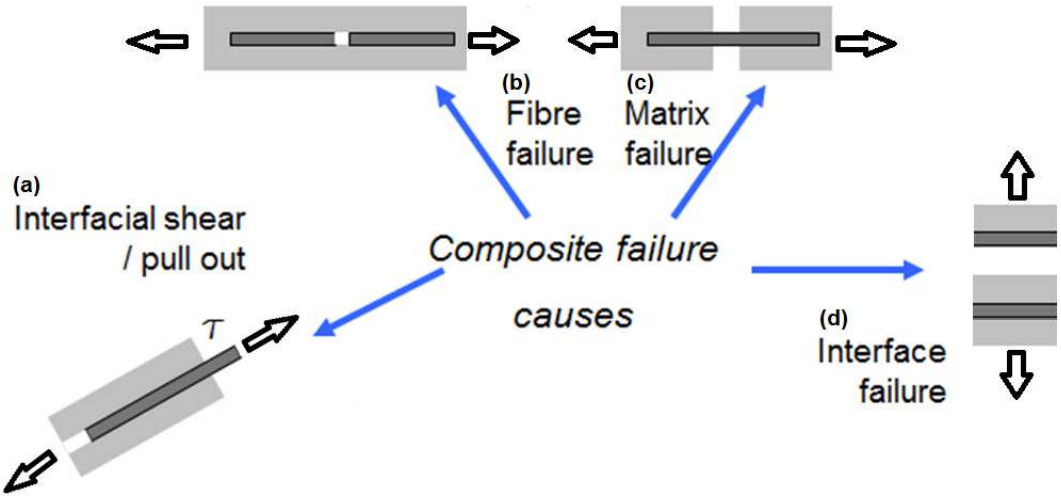


Figure 2-11: Modes of failure in composite systems

2.3. Natural fibre composite

2.3.1. Mechanism of fibre matrix coupling

As mentioned in 2.1.3, cellulose wall is rich with the polar hydroxyl groups. Natural fibres possess a hydrophilic nature while the polymer matrices like PP and Polyethylene (PE) have non-polar hydrophobic nature. The result is a poor interface and a poor adhesion leading to an affinity to absorb water. The coupling mechanism depends on the removal of surface contamination and decreasing the molecular energy at the surface [Muk09]. Figure 2-12 summarises the common treatment methods to get the natural fibre coupled with the polymer matrix.

The chemical treatments depend mainly on exploiting the hydroxyl groups found abundantly in cellulose and hemicellulose. Chemical coupling agents possess two functions; to react with the hydroxyl groups and also to react with functional groups of the matrix [Li07]. However, the chemical bonding theory for the coupling between fibres and thermoplastic is not sufficient to explain different behaviour like increasing the

tensile modulus of other polymers / natural fibre composites [Pet13]. There are other explanations of the coupling mechanisms as listed by Bledzki [Ble99b] like: removal of weak boundary layers; development of a highly cross-linked interphase region between that of substrate and of the polymer; wetting enhancement between the fibre and the polymer; and formation of covalent bonds.

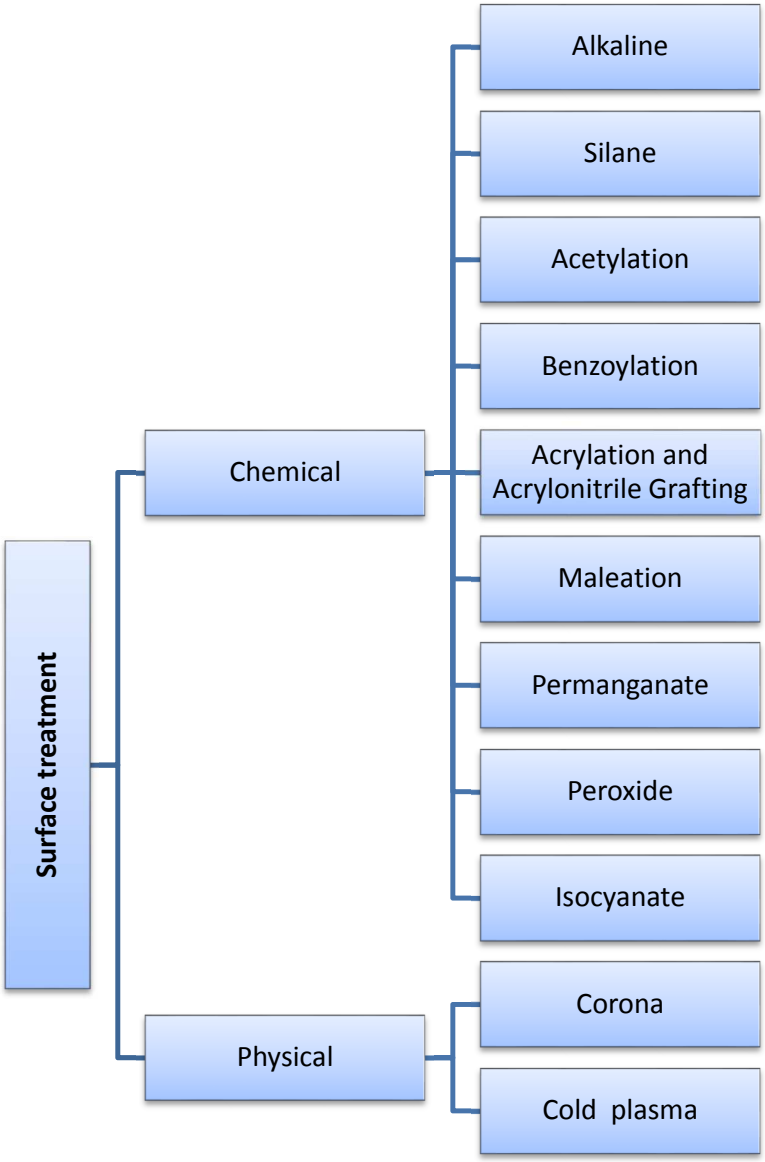


Figure 2-12: Common treatment for coupling natural fibres with a host polymer matrix [Li07] [Rei15]

The most important chemical treatments shown in Figure 2-12 are detailed as follows:

- Alkaline treatment uncovers the fibre surface and works to get rid of lignin, wax and oils. Solution sodium hydroxide (NaOH) to natural fibre promotes the ionization of the hydroxyl group to the alkoxide as shown in Equation 2- 2 [Agr00].

$$Fibre - OH + NaOH \rightarrow Fibre - O - Na + H_2O$$

Equation 2- 2

- Silane treatment functionalise in the presence of moisture. Hydrolysing of alkoxy group like $CH_2CHSi(OH)_3$ leads to the formation of silanols which in turn reacts with the hydroxyl group of the natural fibre, forming stable covalent bonds [Agr00]. The formed hydrocarbon chain $CH_2CHSi(OH)_2$ -Fibre restrains the swelling of the fibre by creating a cross-linked network due to covalent bonding between the matrix and the fibre.
- Acetylation is an esterification method causing plastification of cellulosic fibres. The hydroxyl group in the nature fibre is replaced by an acetyl group, such as Fibre-$OCOCH_3$, which in turn modifies the polymer matrix to possess a hydrophobic nature. Normally silane treatment is a consequent step for the alkalinisation [Hil98].
- Maleation possesses an extra advantage. Maleic anhydride does not modify only the fibre surface but also the polymer matrix to get a stronger interfacial bonding and hence higher mechanical properties [Kee04]. The maleic anhydride is activated at high compounding temperature and thus results in a cellulose esterification. Simultaneously, the surface energy is increased to the level of the polymer surface energy and hence better wettability is achieved. Figure 2-13 shows the coupling between cellulose and a polymer (PP in this case) [Ble96].

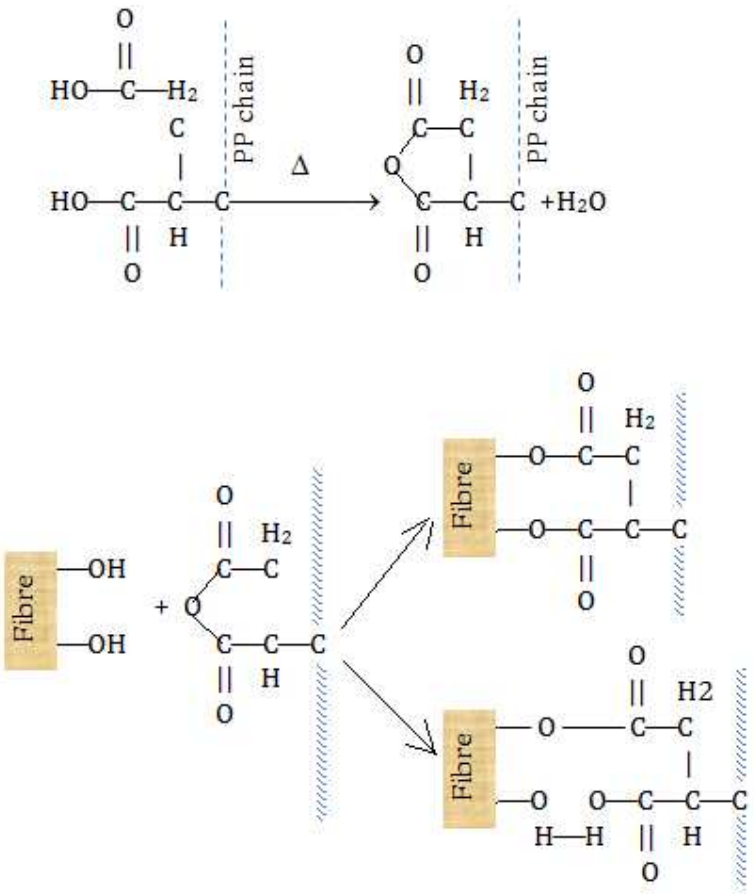


Figure 2-13: Reaction of cellulose fibres with maleic anhydride grafted PP [Ble96]

The physical ways to treat the fibre surfaces as shown in Figure 2-12 are corona and cold plasma treatment. Corona treatment incorporates the activation of the fibre surface and helps in improving the compatibilisation between the polymer and the fibre [Ble02]. In cold plasma, electric discharge is the way to sustain a plasma where the electron temperature is high enough to activate the fibre surface by cleaning, promoting the effect of coupling agents, chemical modification of the fibre surface where free radicals are introduced and cross linking the materials at the surface [Muk09].

2.3.2. Production techniques

Different techniques are used in processing natural fibre composites. It is required to adapt the already available polymer processing techniques for processing these composites.

Figure 2-14 illustrates the techniques mainly used nowadays for producing natural-fibre thermoplastic composites. Thermosetting processes are out of the focus in this work. The status of the product is classified also to semi-finished or finished product [Zie12]. Selection of the production technique is dependent on the available fibre form, the desired production rate and the expected properties. Attention should be also paid

to the definition of processing parameters because wrong parameters selection lead to fibre damage or thermal decomposition and accordingly low mechanical properties, as shown in Figure 2-15 [Zie05].

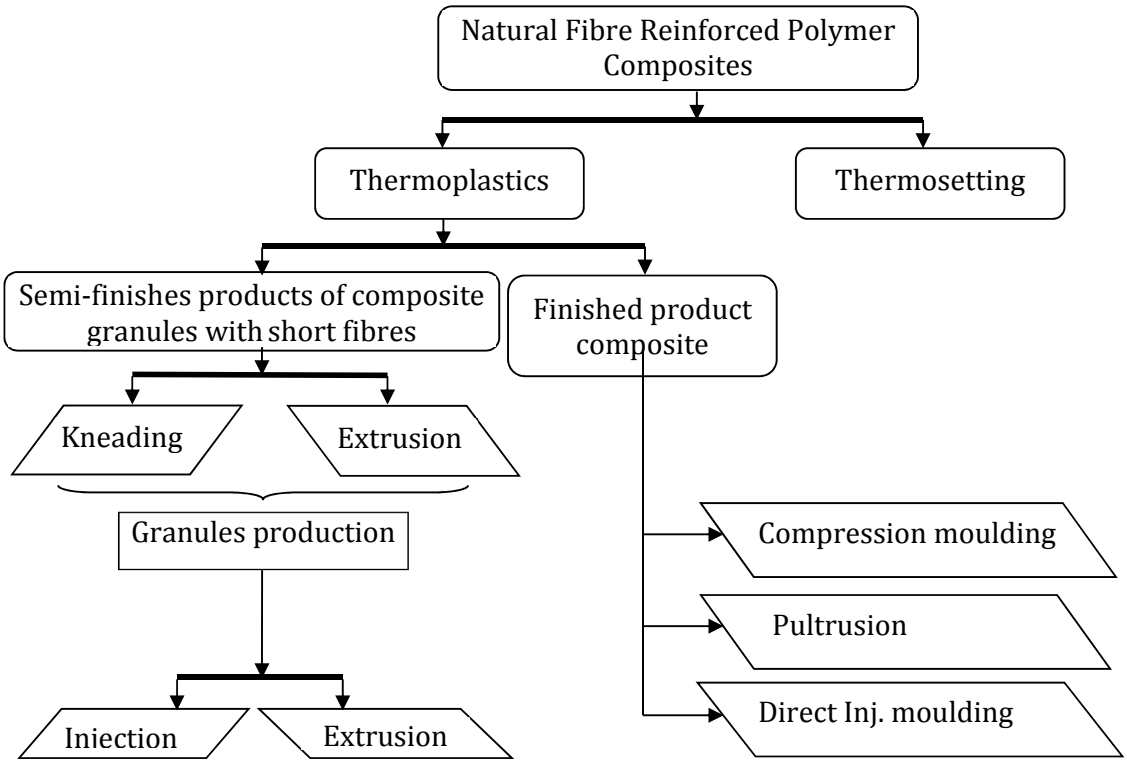


Figure 2-14: Processing techniques for processing natural fibre polymer [Zie12]

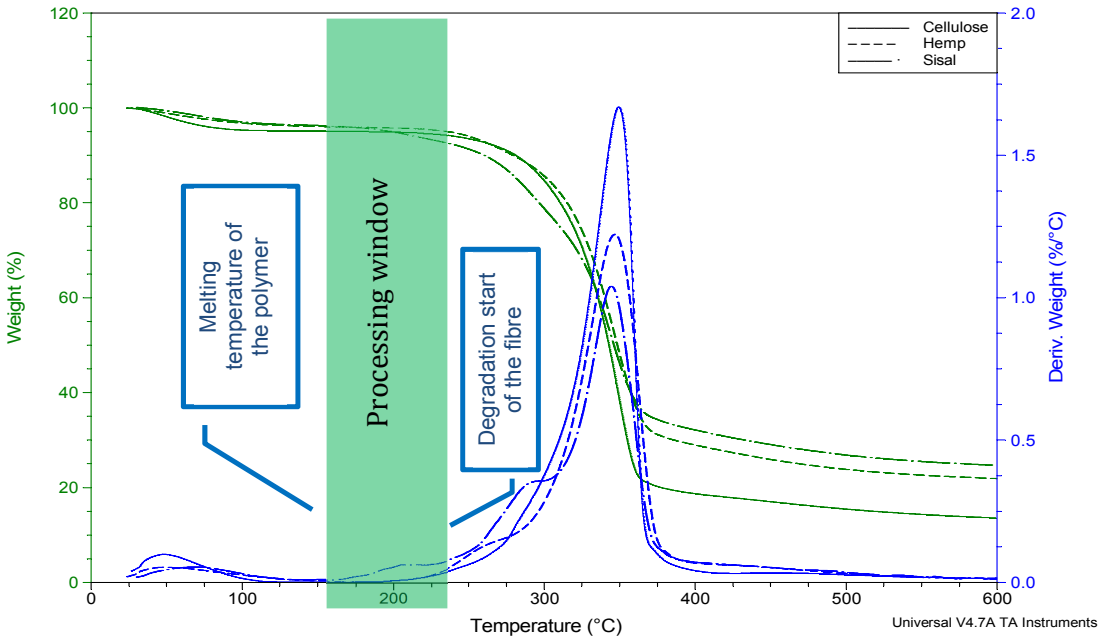


Figure 2-15: Processing window of NFC defined by thermal gravimetric analysis (TGA)

Selection of the production technique depends on the production rate and the product status (semi or finished). Injection moulding requires prepared granules of composites whereas the pultrusion, filament winding and extrusion processes can deal directly with continuous fibres (natural or synthetic) to manufacture a profile-section product. Also the production technique affects the fibre aspect ratio and fibre orientation and hence the mechanical properties are defined. For instance, in pultrusion long and unidirectional fibres are attained within the produced profile. On the other side, more randomness in fibres' directions is attained in extrusion and injection moulding. Figure 2-16 shows the different fibre product forms (raw, sliver, yarn, fleece or felts) and the suitable different manufacturing techniques as well as the effect of fibre technique on the production rate, fibre length and mechanical properties.

This study focuses on the processing of natural fibre thermoplastic composites (NFTC). Therefore more concern will be given on the production techniques of the thermoplastic composites like kneading and extrusion. These processes incorporate the application of both shearing and temperature to ensure a homogeneous distribution of fibres within the matrix.

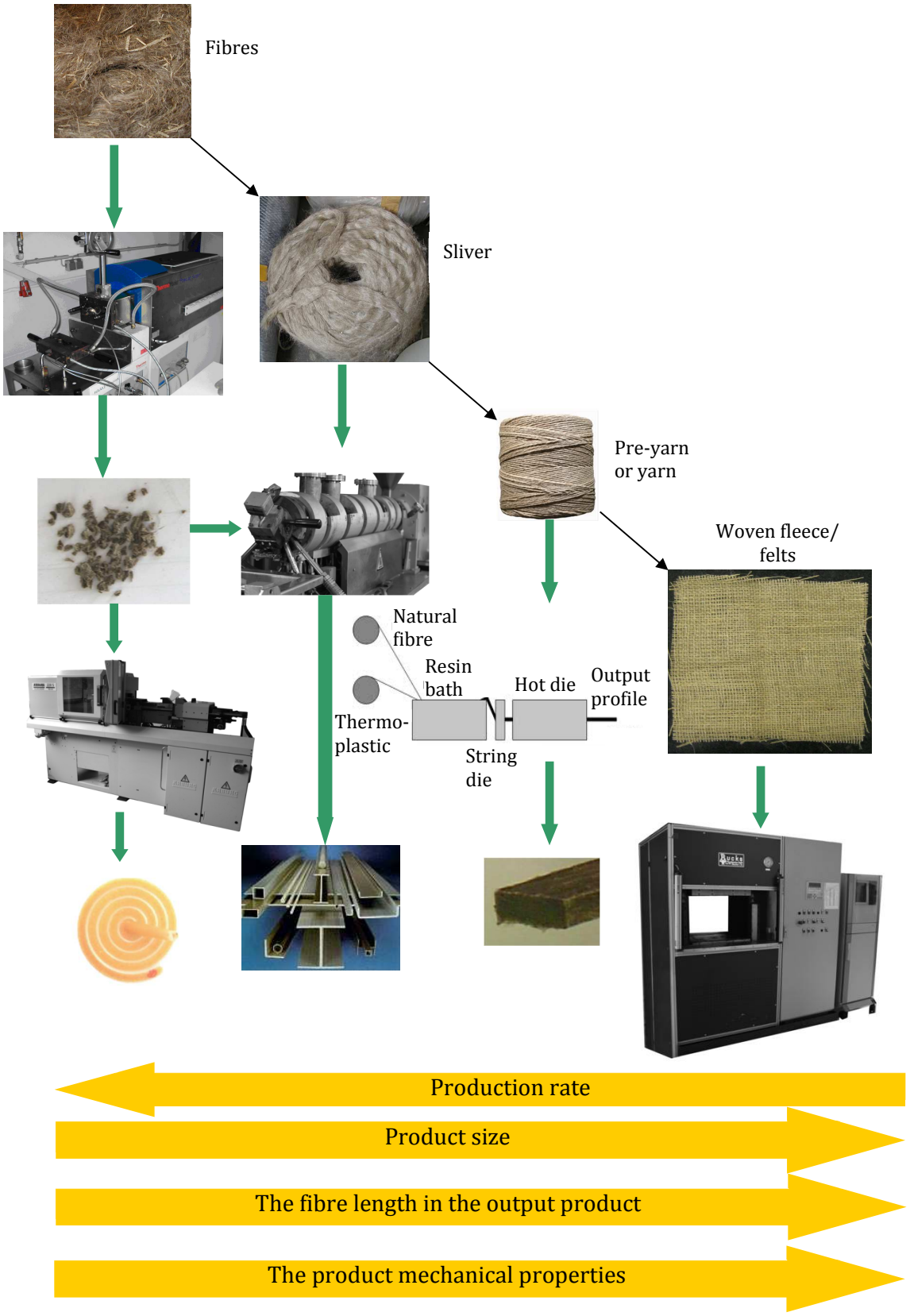


Figure 2-16: Product properties' dependence on Fibre product form / manufacturing technique

2.4. NFTC Properties: mechanical, physical, thermal

The effect of reinforcing thermoplastics with natural fibres on the mechanical, physical and thermal properties is frequently reported in literature. For instance, Shubhra [Shu13] reviewed the effect of different types of fibres on the mechanical properties of PP from other literature [Bar10], [Sam09], [Kar07], [Hay10], [Haq10a], [Haq10b], [Kha10a], [Mue03], [Kha10b] as listed in Table 2- 4. At 10% of fibre content, Flax has the best tensile strength regarding the other types of natural fibres. However it is still away from the performance of E-glass fibre as shown in case of 50% fibre content. The tensile modulus shows better trend for natural fibres where flax again is the best but it is much multiple times of the phosphate glass fibre / PP composite. Jute has also pronounced properties next to flax in tension but better than it in impact. This proves the superiority of bast fibres in tension modus. Regarding strength property, halm fibres like bamboos, fruit and leaf fibres (coir and abaca) are next to bast fibres. The order of composite strength reported in [Shu13] corresponds to the order of fibre tensile strength in Table 2- 3. This evidences the effect of fibre effect and that they are not influencing the overall composites as just filler materials. Other composites made of fibres like coir, palm and calcium aginate are characterised by relatively good bending and impact properties in comparison to the glass fibre composites.

The role of fibre content appears here in the 7% tensile strength improvement by increasing flax from 10% to 50%. Similarly, 19% improvement in strength takes place for bamboos upon increasing from 10% to 30%. Coir does not show significant improvement in tensile and bending strengths upon fibre content increase. However, there are other comprehensive works discussing the effect of fibre reinforcing like [Hai09] and [Han12]. Hai [Hai09] studied the fibre type (jute versus coir) at 50% fibre content reinforced with PP. He used compression moulding and reported very high tensile strength for jute composites. He also correlated the fibre content with the resulting void percent in the produced composite. Han [Han12] studied injection moulded Kenaf reinforced PP and poly lactic acid (PLA) composites up to 40% as shown in Figure 2-17. Improvement of flexural modulus is proved for PP and PLA but it is more remarkably with PP. Flexural strength shows dependence on fibre content only in case of PP. This result proves the role of matrix and the favourable interaction between fibre and PP chain additionally to the PP low viscosity.

Table 2- 4. Mechanical properties of selected natural fibre thermoplastic composites [Bar10], [Sam09], [Kar07], [Hay10], [Haq10a], [Haq10b], [Kha10a], [Mue03], [Kha10b]

PP/Natural fibre system*	Compounding technique	Tensile [MPa]	Tensile modulus [MPa]	Bending strength [MPa]	Bending modulus [MPa]	Impact strength [KJ/m²]
Flax:PP (10:90)	Twin screw extruder	49.5	4138.4			1.9

Wood fibre:PP (10:90)	Tewin screw extruder	33.5		49.22		
Bamboo:PP (10:90)	Twin screw extruder	36.1	728	37.2	1526	
Abaca:PP (10:90)	Single screw extruder	26.7	1661	47.1	1500	
Coir:PP (10:90)	Single screw extruder	27.0	495	36.2	517	5.9
Palm:PP (10:90)	Single screw extruder	25.9	1209	49.3	1526	
Calcium aginate fibre:PP (10:90)	Hot press	24.6	1092	36.0	1371	16.5
Jute:PP (10:90)	Hot press	41.6	714	44.0	2122	11.6
Flax:PP (50:50)	Hot press	53.0				
Sisal:PP (30:70)	Hot press	29,2		48,9		
Bamboo:PP (30:70)	Twin screw extruder	43,0		45,0		
Coir:PP (20:80)	Hot press	28,5		40,5		
Coir:PP (30:70)	Hot press	25,0		38,0		
Jute:PP (50:50)	Hot press	41,5		48,5		
Phosphate glass fibre:PP (10:90)	Hot press	39.3	699	46.3	2587	7.7
E-glass fibre:PP (50:50)	Hot press	85.5	6980	84.6	12007	34.8

*Reference properties for PP with melt flow rate of 52 (tensile modulus=1593 MPa, tensile strength=27 MPa, elongation >600%)

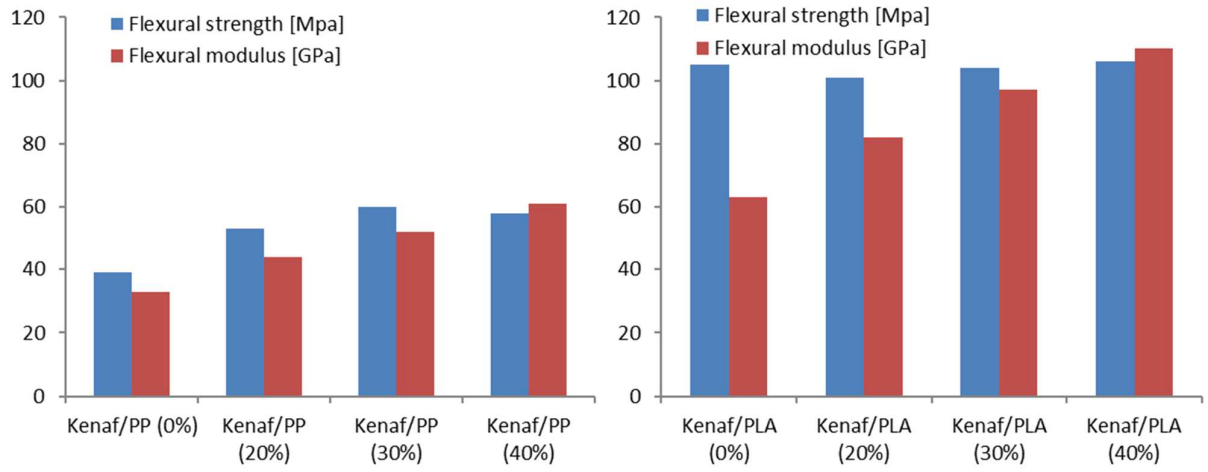


Figure 2-17: Effect of kenaf content on flexural strength and modulus for a- PP b- PLA

Besides to the effect on the mechanical properties, addition of natural fibres has also physical and thermal effects. Physical effects include density, water absorption, acoustic damping etc… More consideration is given in this work to the water absorption

phenomenon. Hai [Hai09], as mentioned above, correlates the fibre content with the evolving void percent. These voids in turn will have more tendency for water absorption. For instance; PP does not absorb water but after being reinforced with 50% Jute and coir, the water absorption rises to 12.2 and 10.0% for jute and coir respectively. These values are reduced to almost 4% after applying a coupling agent. The same behaviour is reported by others like Guduri [Gud07]. Water absorption problem should be treated to avoid product retting (biodegradation) and dimensions change.

The impact of natural fibre addition to thermoplastics on the thermal behaviour is studied with thermal gravimetric analysis (TGA), differential calorimetry scanning (DSC) and dynamic mechanical analysis (DMA). Brief and only important thermal effects of natural fibres on NFTC will be listed as follows:

- Natural fibre has three steps of decomposition which are the humidity at 100°C, the hemicellulose pyrolysis below 300°C and then α-cellulose at almost 350°C according to the type of the fibre [Doa07]. In general, the thermal resistance of natural fibre composite is higher than that of neat PP. This improvement depends also on the efficiency of the coupling agent (type, quantity with respect to fibre content) [El-09c],
- DSC results show that incorporation of natural fibres results in higher melting point due to the restriction of fibres for the polymer molecules flowability during the melting process. Also a linear relationship between cooling rate and crystallization rate was observed [Cui10]. Incorporation of a coupling agent increases the melting point and improve the overall thermal resistance indicating the stronger interface between fibre and matrix due to the formed covalent bonds [Doa07],
- The crystallisation temperature as well as the crystallinity percent of the host polymer in the composites is higher than that of the non-reinforced polymer. This indicates that the fibres act as nucleating agents, hence the host polymer in the composites started crystallizing at higher temperatures [Mof12], [Jos03],
- DMA analysis proved also the increase in storage modulus upon increasing the fibre content. This is attributed to restriction in the segmental motion. This is evidenced by the higher glass transition temperature in the composites [Mof12] [Doa07].

2.5. Review about the role of fibre length, orientation and straightness

The influence of fibre length and orientation on the composite mechanical properties is illustrated in Equation 2- 3 where Vf is the fibre volume fraction, σf, σm are strength of fibre and matrix respectively, η_o and η_l are the orientation and length factors. Equation 2- 3 is a modified role of mixture for the composite tensile strength. Equation 2- 4 defines the length factor in terms of the critical fibre length presented in Equation

2- 5. The strength component related to fibres increases with the increase of the fibre aspect ratio. High aspect ratio guarantees higher load transfer by the fibre. Similarly, as the fibre orientation, defined in Equation 2- 6, increases, the fibre strength component decreases, as reported by Pan et al [Pan93].

$$\sigma_c = \sigma_m (1 - v_f) + \eta_o \eta_l \sigma_f v_f$$

Equation 2- 3

Efficiency terms for the fibre length are defined in Equation 2- 4. Figure 2-18 shows the effect of fibre length with respect to the fibre critical length (fibre length or aspect ratio at certain diameter corresponding to the maximum load transfer)

$$\eta_{l\sigma} = \begin{cases} 1 - \dfrac{l_c}{2l} \cdots l \geq l_c \\ \dfrac{l}{2l_c} \ldots l < l_c \end{cases}$$

Equation 2- 4

l_c is the critical fibre length at which the fibre loading efficiency is maximised. It is defined in Equation 2- 5.

$$l_c = \frac{\sigma_f d}{2\tau}$$

Equation 2- 5

σ_f is the fibre strength, d is the fibre diameter and τ is the interfacial shear strength.

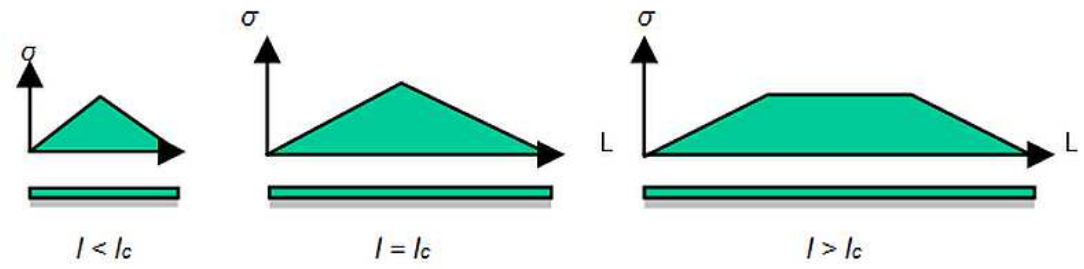


Figure 2-18: Effect of fibre length on fibre capacity for load transfer.

$$\eta_o = \sum_n a_n \cos^4 \phi_n$$

Equation 2- 6

Where a_n represents the fibre fraction of Φ_n. For in-plane random distribution η_o is 0.375 and 0.2 for 3-d distribution.

The composite overall E-modulus can also be described in an equation similar to that of the composite strength Equation 2- 3. The orientation factor is the same as defined in Equation 2- 6. But the length factor is defined as illustrated in Equation 2- 7.

$$\eta_{lE} = 1 - \frac{\tanh(\beta l / 2)}{\beta l / 2}$$

Equation 2- 7

where

$$\beta = \frac{1}{r_f}\sqrt{\frac{2G_m}{E_f \ln(R / r_f)}}$$

Equation 2- 8

'r_f' is the fibre diameter and R is the inter-fibral distance based on homogeneous geometrical packing. E_f and G_m are the fibre elastic and the matrix shear moduli respectively. The value of R / r_f is related to v_f as in Equation 2- 9.

$$R / r_f = \sqrt{\frac{\pi / 4}{v_f}}$$

Equation 2- 9

Most of the researchers used the mean values of the fibre lengths [Kel65], [Bos04], [Gla99], [El-14c]. But Andersons [And06] has used Weibull distribution in order to describe the fibre length population. Hence, the fibre portions below and above the critical fibre length can be defined. Andersons investigated extruded flax roving-polypropylene composites at 180-200°C using twin screw extruder. However, this mixes the both effects of fibre shearing during extrusion and the fibre fragmentation/ fibrillation due to the high temperature.

Beaugrand [Ber14] avoided the effect of thermal decomposition on the fibre size. He carried out experiments on low melting polymer polycaprolactone (PCL) with 20 wt% chopped Hemp fibres to avoid fibre thermal decomposition.

Fibre straightness whether it is straight or tangled, does not receive a great attention in the previously mentioned studies, although it is believed to have such as also a great role in describing the overall mechanical properties of the composite.

2.6. Functional additives to NFTC

NFTC, as normal polymers, require functional additives like:

- Coupling agents for binding the fibres with the host thermoplastic polymer,

- Impact modifiers or plasticizing agents for increasing the energy needed to break,
- Pigments for colouring,
- Ultra violet (UV) stabilizers and antioxidants to avoid the release of organic peroxides which in turn degrade the mechanical properties,
- Lubricants to avoid the sticking of the material to metal surfaces and lower the amount of energy needed in processing.

Concern will be given to the impact modifiers and flame retardants because they are studied in this work comprehensively.

2.6.1. Impact modifiers

A very important drawback of NFTC is the low toughness and the corresponding reduced impact strength which arouse the need for investigating different ways for impact strength improvement.

Both the natural and synthetic rubber (ethylene propylene diene monomer EPDM) are used as elastomeric substances to improve the polypropylene PP composite filled with 20 wt% vetiver grass [Ruk09]. Different portions of the rubber in the range of 0-50 wt% are added with respect to the composite. The impact strength and the elongation of the composite are enhanced for rubber content more than 10%. On the other hand, the strength and the young's modulus fall tremendously below the pure PP values. Up to 10% rubber, the mechanical strength and tensile modulus are kept with insignificant improvement in impact strength and elongation. It should be taken into account that the viscosity is raised with the application of rubber. It is important to mention that natural rubber has slightly lower viscosity in comparison with the effect of EPDM. The same way of impact strength improvement is followed by Manchado et al. [Lóp03]. 20 and 30 wt% of EPDM are added to PP 20% flax composite. Significant improvement and elongation are attained with EPDM. However, the tensile strength deteriorates in comparison to the non-treated composite. It is claimed that EPDM also enhances the nucleation and crystallisation process. Apparently, the quick crystallisation and better adhesion can be attributed to the maleic anhydride grafted PP.

Oksman et al. [Oks03] attempted to improve the bio-composite impact strength of Polylactic acid PLA filled with 40 wt% flax using the triacetin. Triacetin enhances the PLA impact strength with 20-26% when treated with triacetin at 5-15 wt%. Compounding is carried out by a twin screw extruder. However no significant improvement in impact strength is recorded; adversely a 1-3% decrease is measured. It is concluded that the addition of Triacetin plasticiser is not positive regarding the composite impact strength properties [Oks03]. This negative result is attributed to a weaker fibre structure upon the addition of triacetin. However, this conclusion may not apply for natural fibre thermoplastic composites containing coupling agents that strengthen the fibre matrix interface. Also, the deterioration in mechanical properties

may be attributed to the low portion of PLA remaining after the addition of 40% flax and 15% triacetin.

Glycerol is used as a plasticiser with natural fibre [Sai08] and wood fibre composites. As reported in [Sai08] , only 3% glycerol is added to the blend of wood PP composite. But in case of natural fibres, glycerol is added in an equivalent quantity to the natural fibre. Glycerol shows better results regarding the values of impact [Sai08] and elongation [Taj08].

Away from the previous three chemical ways, the addition of another type of natural fibre can induce an improvement in the impact strength for two reasons; either the fibril angle or the cellulose content [Gra09]. Cellulose is the main load bearing element in the composite system besides to the quality of the interfacial adhesion. Reich-Albrecht [Rei10] uses the natural nettle fibres which is characterised with its high cellulosic content. Graupner et al. [Gra09] attempted to combine the effect of high fibril angles like cotton and man-made lyocell cellulosic fibres with the low fibril angle like bast fibres. As a result, composites of better impact strength and strength are achieved.

In this study, different methods will be focused on improving the impact strength property of the natural fibre composites PP/Flax system.

2.6.2. Flame retardants

Flame retardant additives to NFTC are essential to enhance their marketing chances especially in the construction, automobile and E&E applications. Data about the sensitivity of NFTC to flame are insufficient [Sai04]. Even Brosius [Bro06] reported that the NFRP excluded from most aircraft, rail and subway markets until the issues of flame, smoke and toxicity are resolved. The use of these composites requires that they should pass regulatory safety tests such as IEC regulations for electrical appliances, ASTM E 108, UL 1256, ASTM D635-98 (UL94), EN 1187 for building, roofing and decorative materials as well as DIN 5510 for low toxic material in the confined areas especially in transport applications.

The flammability behaviour of NFTC is governed by the polymeric matrix and the fibre type. This work deals with the degradation of thermoplastics especially polypropylene. PP with its aliphatic structure degrades normally by random scission due to the presence of hydrogen atoms on all carbon atoms [Bla04] hence resulting in flammability. Coupling agent such as maleic anhydride-grafted-polypropylene (MAPP), which is normally used for linking PP and the natural fibres, helps in suppressing the flame. The cyclic anhydride structures are prone to slow down the hydrolysis and thus results in intramolecular cross linking of the polymer chains [Kan08].

Furthermore, the flammability of natural fibre is governed by a number of factors, namely fibre constituents (lignin, cellulose, hemicellulose, pectin, waxes, etc…), the combustion characteristics of the released organic volatiles during decomposition, degree of cellulose polymerisation and fibre orientation [Koz08] [Cha10a]. Lignin releases less volatiles and thermally decomposes at temperature greater than those of hemicellulose and cellulose. Lignin starts to decompose normally by breaking weak

bonds at relatively low temperatures (i.e. 160°C for flax) [Cha10a]. It continues its decomposition and cleavage of the bonds in its aromatic ring starts at high temperature (i.e. almost 400°C for flax). Accordingly, higher amount of lignin lowers fibre decomposition temperature. Also according to Manfredi et al [Man06], lower content of lignin is desirable in order to delay the ignition start time. However the aromatic rings present in lignin resist fibre oxidation. Increase of lignin percent results in the increase of char formation more than cellulose and hemicellulose do.

Cellulose is also considered to be more flammable because it produces volatile flammables 'Levoglucosan' [Koz08] [Bas77]. Hemicellulose, which decomposes early in the 200-260°C range, has less contribution in forming combustible gases. An increase in crystallinity results in more levoglucosan during pyrolysis, which requires more activation energy to imitate pyrolysis [Lew05]. Finally, more fibre orientation results, assumedly, in less oxygen permeability in fibres and hence flammability resistance is improved [Lew78].

Therefore flame retardant (FR) materials are necessary in order for them to be suitable for a wider range of applications. However, it should be considered that the implementation of such retardants might results in negative aspects that might compromise the mechanical properties [Sai04]. Flame retardance and mechanical behaviour are necessary for composites. Flame retardance is more effective if it can stop the ignition process during one of its steps; namely heating, decomposition, ignition, combustion and propagation [Sai04] [Bas77]. Kozlowski et al. [Koz04] reported that this objective can be achieved by impregnation of the fibres with flame retardants (FR) before compounding, or by implementation of FR during manufacturing processes or by insulation of the composite product in the finishing stages with intumescent materials in order to prevent the penetration of heat.

Flame retardance, in general, can be employed either by chemical or physical mode of actions [Fin04]. Physical mode flame retardation mechanism takes place either by cooling resulting from the endothermic reactions accompanying by the metallic hydroxides degradation such as aluminium trihydrate (ATH) or Magnesium hydroxide ($Mg(OH)_2$) due to its relatively higher thermal stability. Secondly for physical mode of action is by forming a protective layer when the additive flame retardant forms a shield with low thermal conductivity upon exposure to heat flux, i.e. phosphorous additive [Fin04] It is reported [Fin04] that almost 75% of the flame retardance industry for the polyolefins uses the metallic hydroxide technique. This is attributed to the possibility of reaching the V-0 rating in UL94V test. Not only is this, but the smoke emission during burning also reduced. Interestingly, it is reported [Sai04] that the use of boric acid or zinc borate will have a synergetic effect with [Sai04] $Mg(OH)_2$ that can result in an excellent behaviour [Sai04]. However lower LOI and horizontal flame speed are obtained in comparison to the $Mg(OH)_2$ treated composite without any other additive. Also the tensile and the flexural properties attained of the fibres treated with $Mg(OH)_2$ are reduced by almost 15% [Sai04].

The current work aims to investigate the application of FR in one of the most widely produced natural fibre thermoplastic composite systems, which is the flax/PP. Flax is

known for its high cellulosic content, high strength, low cost, low density and its recyclability [Hel00], [Tah06], [Arb05], [Bos04]. For flame retardance, only magnesium hydroxide is considered in this study. Other types of FR are not considered as published in previous literature [Sch03], [Le 05]. The following points, namely the fibre content, FR content and number of injection cycles, are considered in this study.

3 Systematic Approach of Experiments

The experimental approach followed in this study aims to solve the problems encountered in the compounding of NFTC with a special concern on PP/flax composites. This work discusses the NFTC production steps starting from the fibre treatment till the properties tailoring by fibre sizing, process parameter selection and functional additives.

3.1 Study structure

Based on Figure 1-3, the concept of the study sequence in this work is designed. The thesis will focus on the linear sequential steps shown in Figure 1-3 to odder a recipe how to optimise the behaviour of the natural fibre reinforced polypropylene. The feedback effects are not considered to make it easy for the reader to follow the different aspects controlling the quality of NFTC. Figure 3-1 shows the one-way structure of this study. Four main objectives, with different designated colours, are under consideration namely: A- Treatment of natural fibres and thermoplastics and coupling agents, B- Definition of the compounding process parameters, C- Injection moulding study with respect to the mechanical properties and the flowability besides to its modelling and D- Effect of the functional additives like impact modifiers and flame retardants.

- A1- Selection of pre-treatment/ modification/ coupling agent:
  Flax natural fibres were treated using trimethoxyvinylsilan (TMVS) and acrylic acid (AA). On the other side, the PP matrix is also treated with different coupling agents; namely, maleated PP (MAPP), (TMVS-MAPP), and acrylic acid-functionalized PP (AAPP).
- A2- Investigation of the selected treatment:
  After selecting a suitable treatment or coupling regarding output mechanical properties, price and environmental impact; the selected coupling agent will be optimised regarding its quantity with respect to the studied property (tensile strength, tensile modulus or impact) and the natural fibre type.
- B- Definition of the compounding process parameters:
  Both kneading and extrusion are studied. However, extrusion is the required compounding technology due to its mass production capacity. Optimisation of extruder configuration is important for the output quality, homogeneity, coloration and of course the final mechanical properties. Not only is the configuration studied but also the processing parameters like fibre content, temperature and shear rate. Are the extruder configurations as well as the processing parameter having also an effect on the NFTC granules which are afterwards injection moulded? This question will be answered in this corresponding section.
- C1- Study of injection moulding parameters with respect to the mechanical properties of the injected NFTC:

The injection pressure, melt temperature, mould temperature and injection speed are the investigated parameters in this study. Back pressure is taken as a constant percentage of the injection pressure (80%). In this point and to ensure enough amount of reproducible properties of the supplied material, commercial products will be used in this part of study.

- C2- Study of the injection moulding parameters with respect to the flowability and the homogeneity of fibre distribution of the injected NFTC:
  The same parameters mentioned above will be studied concerning the flowability length in a spiral injection mould. Additionally, the fibres are extracted from the injected samples to determine the actual fibre content along the spiral and hence assess the quality of fibre distribution.
- C3- Modelling the NFTC flowability and fibre distribution patterns:
  Understanding the change in fibre content and fibre length with respect to the applied injection parameters as well as the fibre type needs an analytical explanation. One dimensional mould is used in this analysis namely, the spiral mould, to follow the development of fibre content in case of 1-D incomplete filled injection mould. The results will be extrapolated for other cases like completely filled moulds and two dimensional flow patterns.
- D1- Improving the impact strength of NFTC:
  In this section different approaches will be tried to enhance the impact strength of NFTC namely, the addition of elastomers, plasticiser and even the addition of another fibre type with improved aspect ratio and cellulose content.
- D2- Flame retardants in NFTC:
  Flame retardants of different types (Inorganic hydrates, halogenated, halogen-free intumescent, etc.) are applied to get more applicable products. A comprehensive study for different FR classes and fibre types is indeed an issue of the moment to characterise NFTC regarding both mechanical and flame resistance is a current challenging issue of the moment. Hence, the market of NFTC can be enlarged.
- D3- Optimisation of FR content regarding mechanical properties for NFTC:
  Implementation of FRs results in another problem which is the drop of the corresponding mechanical properties. Besides, it is also aimed to increase the share of the ecological types of flame retardants such as the mineral inorganic hydrates. Therefore, a study is needed to optimise the flame retardance level (UL94 and cone calorimetry tests) with respect to the mechanical properties and the ecological FR share.

Each of the previous four mentioned objectives will be discussed in a separate section in this study. Therefore each section will have its own subtitles of introduction, experimental work, results and discussion.

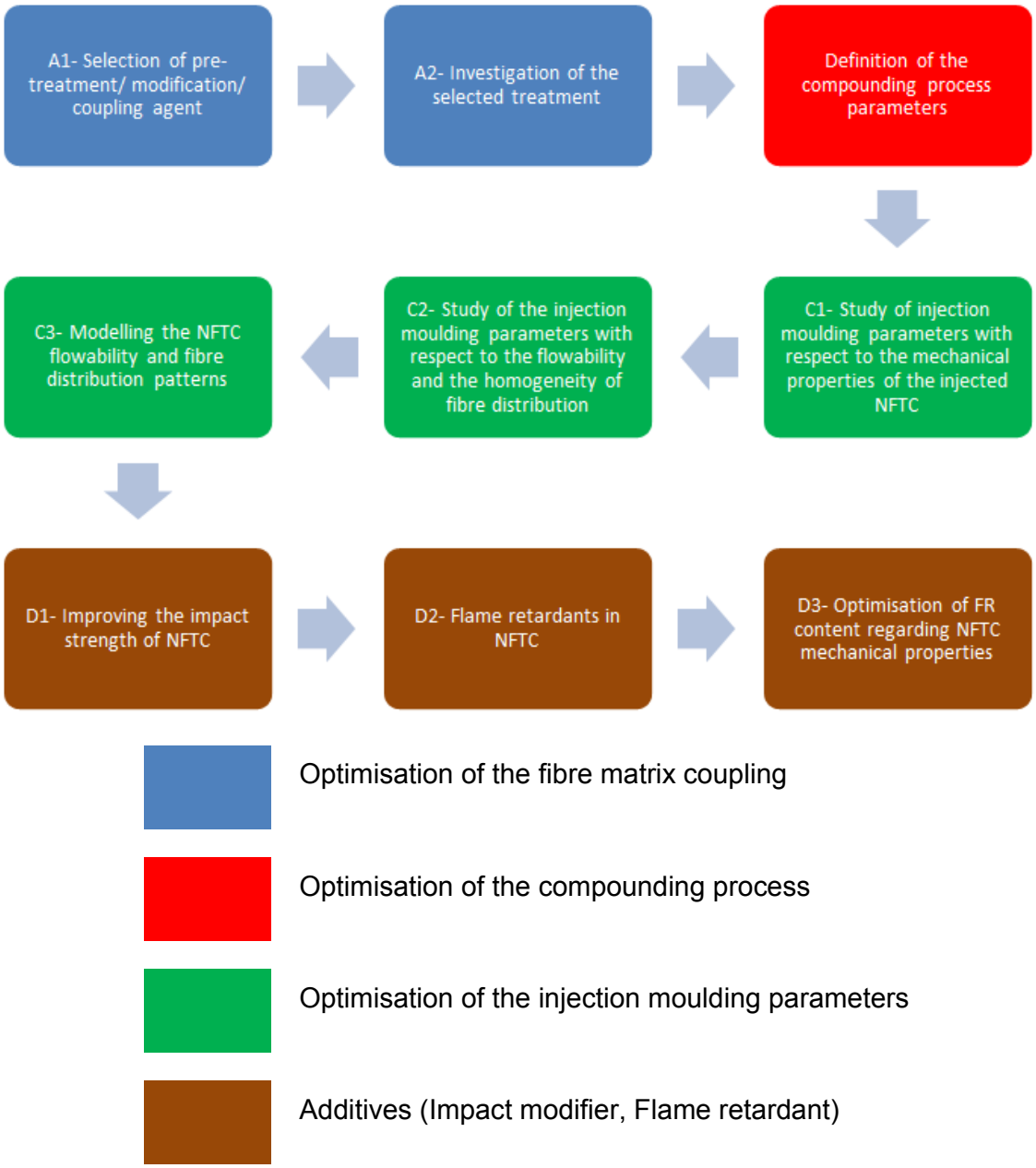


Figure 3-1: Research steps in this study

Every optimisation step needs a compounding process of a sample with the investigated conditions and the corresponding testing procedure. Figure 3-2 presents the input material and the selected treatment in this study, the planned compounding techniques as well as the influencing parameters and the subsequent criteria of characterisation:

- Input materials (Polymer,Natural fibres and additives).
- Compounding process with the affecting parameters (shear rate, temperature, compounding time and fibre content).

- Testing and evaluation with respect to different aspects such as mechanical, water absorption, thermal analysis and homogeneity of fibre size).
- Feedback on the next compounding trial.

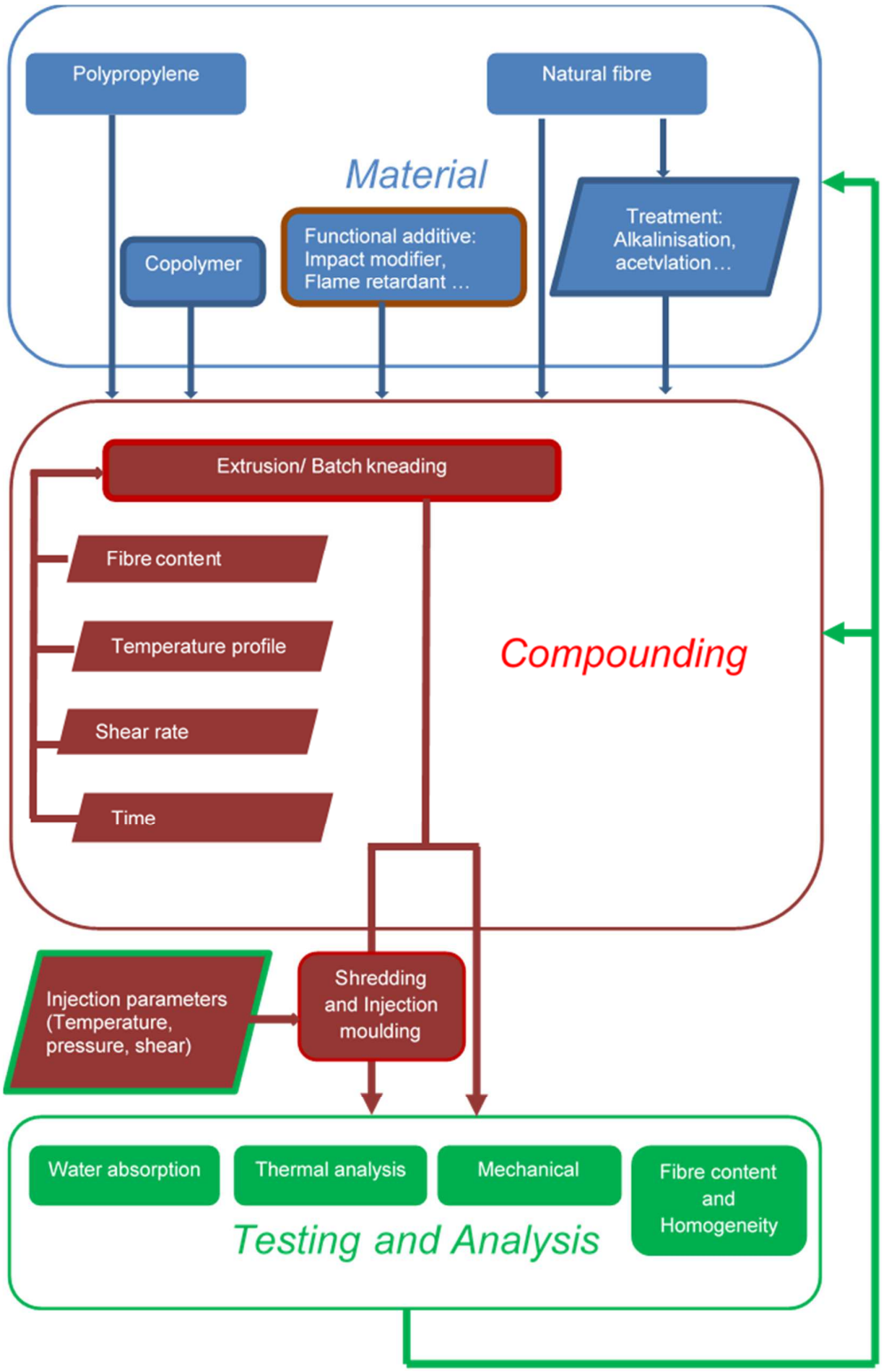


Figure 3-2: Work packages (Coloured frames are linked to the coloured blocks in **Figure 3-1**

3.2 Materials

3.2.1 Natural fibres

Table 3-1 lists all the types of natural fibres used in the whole study. All fibres are used for reinforcing the host polypropylene matrix except for the nettle which is mixed with flax fibres, in the this study, for the sake of impact improvement as will be described later in chapter 7.

Table 3-1. Used natural fibres in the study

Natural fibre	Supplier	Notes
Flax	Sachsenleinen GmbH Germany	Sliver form*. The lengths of technical fibres vary from 100 to 500 mm and diameter of 68 µm in average. The constituents are cellulose 63%, hemicelluloses 16%, pectin/lignin 4%, fats and waxes 1%, proteins/ash/minerals 4%, and water content 12%
Hemp	Sachsenleinen GmbH Germany	Sliver form. The constituents are: cellulose 65%, hemicellulsoe 16%, pectin/ lignin 4%, fats/ waxes 1%, proteins/ashs 2% and water 12%,
Sisal	Sachsenleinen GmbH Germany	Long fibres form*. The constituents are: cellulose 63%, hemicellulsoe 12%,pectin/ lignin 11%, fats/ waxes 1%, proteins/ashs 1% and water 12%.
Jute	Sachsenleinen GmbH Germany	Long fibres form*. The constituents are: cellulose 62%, hemicellulsoe 13%,pectin/ lignin 13%, fats/ waxes 1%, proteins/ashs 1% and water 10%.
Nettle**	stoffkontor kranz AG in Lüchow-Dannenberg	Sliver form. 92% cellulose**
F25***	FIBERGRAN GMBH	is a commercial granules supply characterised with good flowability, aging resistant and thermal stability properties
Cellulose	Cordenka	length = 0,5mm
Cellulose	Cordenka	length = 1,5mm
Hemp Pellets	BaVe Badische Faserveredelung GmbH, Malsch)	Original fibres from France
Flax Pellets	BaVe Badische Faserveredelung GmbH, Malsch)	Original fibres from Netherland
Sisal	BaVe Badische Faserveredelung GmbH, Malsch)	Fibre bundles supply from Cayetano Garcia Del Moral S.L., Cabra del Santo Cristo, Spanien and pellets pressing in BaVe
Wheat straw	USA	--

Kenaf Pellets	BaVe Badische Faserveredelung GmbH, Malsch)	Original fibres from Bangladesh
Wood fiber, Arbocel B 800	Rettenmeier & Söhne GmbH & Co. KG, Rosenberg	Average Length 130 µm and diameter 20 µm

* In case of kneading, the fibres are chopped into almost 30 mm length

** The reported cellulose content is according to internal analysis

*** FiberGran is not a pure fibre but already mixed NFTC of 25% Flax and 75% PP

3.2.2 Thermoplastics

Polypropylene DOW H 734 52 RNA supplied by Dow Customer Information Group, Edegem, Belgium. Melt flow index of this homopolymer at 230°C and at 230°C/2.16 kg is 52 g/10 min, specific density of 0.9.

3.2.3 Coupling agents

Table 3-2 presents the different coupling agents selected in this study for preliminary investigations.

Table 3-2. Prepared coupling agents

Coupling agent type	Supplier	Notes
MAPP (prepared by grafting MA M625 powder)	Sigma-Aldrich.	by mixing PP with maleic anhydride in a weight ratio of 98:2 and then 1% of the peroxide catalyst is added*. This mixture is extruded at 180°C and 40 rpm. Then the resultant is mixed mechanically with PP at 5% weight fraction using kneader Haake Rheomix 600P. After the screening study for selecting a coupling agent, another two commercial products of MAPP were tried for further investigation namely: • MAPP supplied by Sigma Aldrich in granulated form with 0.934 specific density at 25°C, Maleic anhydride content =8-10%, viscosity 4.0 poise, melting point of 156°C, acid number of 47 mg KOH/g • Carboxylated PP (Maleic Anhydrid) Scona TPPP 8112FA supplied by Kometra with specific density of 0.91, MFR (190 °C/2,16 kg) > 80 g/10 min, melting point of 155-170°C, maleic anhydride content =1.4% in powder form.
TVMS-MAPP	TVMS is supplied by Merck Schuchardt	TMVS is mixed with MA, peroxide* and PP with the ratio of 4.5:4.5:1:90. The mixture is then extruded at 180°C and 200 rpm. Finally, the mixture is cooled and pelletized.

AAPP (prepared by grafting AA)	Merck Schuchardt	Molecular wt= 148.23 g/mol Acrylic acid is mixed with PP in ratio of 3 : 97 and then extruded together at 180°C and 200 rpm. And then, the mixture is cooled and pelletized.

* peroxide 90% ‘‘Luperox 101 in. is supplied by Sigma-Aldrich

3.2.4 Impact modifiers

For the sake of impact strength improvement, the listed chemicals in Table 3-3 are used. The addition of a plasticiser and an elastomer is carried out.

Table 3-3. Used chemicals for impact modification

Impact modifier	Supplier	Notes
Triacetin (C9H14O6)	Sigma Aldrich, Germany	Plasticizer : CAS 102-76-1 with molecular weight of 218.2 g/mol
ethylene propylene diene monomer EPDM	Milos GmbH, Melle, Germany	Elastoemr with size of 0.0-0.5 mm Powder form Red in colour

3.2.5 Flame retardants

Table 3-4 lists all the used materials to impart flame retardant property for the prepared NFTC. These materials are either flame retardants (Magnesium hydroxide, aluminium trihydrate, ammonium polyphosphate, decabromodiphenyl oxide) or synergists (nanoclay, antimony trioxide, zinc borate) to improve the resistance to the fire. Table 3-5 shows the both types applied of Exolite FR. AP-766 is suitable for PP, PE, PP copolymers and PP blends for injection moulding and extrusion applications. AP-422 is characterised with its reduced solubility in water, lower viscosity in aqueous suspensions, very low acid number (Max 1 mg KOH/g) and it is eligible for wood plastic composites (WPC) [Ble08].

Table 3-4. Used flame retardants and synergetic materials

Flame retardant/ Synergist	Supplier	Notes
Magnesium Hydroxide	Sigma-Aldrich, Germany	Flame retardant: CAS number 1309-42-8 (purum p.a. grade)
Aluminium trihydrate	Nabaltec	Apyral 60CD
ammonium polyphosphate	Clariant, Germany	Flame retardant: non-halogenated flame retardant based on phosphorus and nitrogen synergism as listed in Table 3-5, Exolit AP-766.

Decabromodiphenyl oxide DECA	Sigma-Aldrich, Germany	Flame retardant: $C_6Br_5OC_6Br_5$ with molecular Weight 959.17
Nanoclay (Sodium montmorillonite)	Sigma-Aldrich, Germany	Synergist: Nanomer® 1.44P, clay surface modified with 35-45wt.% dimethyl dialkyl (C14-C18) amine
Antimony trioxide Sb_2O_3	Sigma-Aldrich, Germany	Synergist: Puriss p.a. CAS number 1309-64-4 and Molecular Weight 291.52

Table 3-5. Main properties of Exolite flame retardants

Property	AP-766	AP-422
Phosphorus [wt.-%]	23-25	31-32
Moisture [wt.-%] Thermogravimetry (infrared lamp)/ 130°C	Max 0.5	Max 0.25
Nitrogen [wt.-%]	14.4-16.4	14-15
Decomposition Temperature [°C]	>275	>275
Bulk density [g/cm^3]	0.6	0.7
Density [g/cm^3]	1.6	1.9

3.3 NFTC preparation

3.3.1 Batch kneading

PolyLab-System Rheomix 600p from (Thermo Haake) is appropriate for natural fibre compounding with the host polymer and the required additives. The system contains co-rotating roller rotors with in a chamber of 69 cm^3 volumetric capability. The maximum rotating torque is 160 Nm. Temperature and speed are adjustable up to 450°C and 250 rpm respectively. The temperature / speed parameters will be illustrated in every section.

3.3.2 Extrusion

The compounding process takes place in Berstorff ZE25 twin corotating extruder. It contains 9 heating zones. Extruder diameter is 25 mm. Speed is up to 1200 rpm. Maximum rotating torque is 90 Nm. Temperature is adjustable up to 400°C. Melt pressure is up to 300 bar. The screw is segmental so that the shearing effect can be

controlled along the extruder. The control of fibre content in the compounded NFTC will be explained later.

3.3.3 Hot pressing

Hot pressing can be useful in NFC preparation of polymers reinforced with natural fibre fabrics. Therefore hot pressing is not used to prepare NFTC in the current study. It is just applied on the extruded NFTC strands for further study of mechanical properties. The NFTC strands are laid longitudinally in a rectangular mould then hot pressed at 500 bar and 200°C. The process proceeds at two steps and in between the load is released to get off the enclosed gases.

3.4 Testing samples preparation by injection moulding

3.4.1 Mechanical testing: Tension and impact (DIN EN ISO 527-2 and DIN EN ISO 179/1eU)

Tensile test of single elemental fibres was carried out according to DIN 53816 for 50 single fibres as shown in Figure 2-9 using a load cell of 20 N. On the other side, tensile testing of the NFTC samples require previous preparation which can be either hot pressing or injection moulding. Hot pressing is according to 3.3.3. Injection moulding requires dried granules (shreddered NFTC) to be injected at a temperature pattern of 185–190–195–200°C (unless otherwise mentioned) using Allrounder 220C 600–250, Arburg, Lossburg, Germany. The injected or pressed samples were then conditioned at 23°C and 50% relative humidity for at least 88 hours, according to ISO 291. Tension tests were made using Zwick universal testing machine equipped with load cells of 2.5 kN and 100 kN, according to DIN EN ISO 527-1. Test sample was injection-moulded according to ISO 527-2. Test was conducted and evaluated according to ISO 527-1.
Impact samples were also injection moulded with the same parameters and received the same conditioning before testing. Impact test is applied on the wide side according to DIN ISO 179/1 for Charpy testing.

3.4.2 Thermal tests: TGA, DSC and DMA

TGA is conducted using Q5000 IR from TA instruments in oxygen or nitrogen atmosphere (as will be mentioned in each section) with 10 k/min rate from the room temperature up to 800°C.
Differential scanning calorimetry DSC test is applied using DSC Q2000 by heating from 25°C to 250°C at 10 k/min rate (unless otherwise mentioned) to observe the melting temperature, recrystallization temperature, melting enthalpy and recrystallization energy of the composites.
Dynamic mechanical analysis (DMA), using Q 800 was done by TA instruments, was carried out on 17.5X10X3 mm^3 samples to monitor the composite characteristics (storage modulus and damping factor). The cantilever loading was set at 1, 10 and 100 Hz frequency and 0.1% strain in temperature range of 40–160 °C and heating rate of

2°C/min. Storage modulus (E'), loss modulus (E'') and mechanical loss factor (tan δ) were measured during the test and plotted as functions of temperature.

3.4.3 Microscopic investigation (Optic and SEM)

Microscopic examination is carried out using a digital microscope from Keyence Corporation, Osaka (Japan) Typ: VHX-500 F with magnification up to X1000. Scanning electron microscope SEM is also used to study the fracture surface of the tensile and impact samples to check the following:

- Quality of fibre adhesion to matrix
- Fibre homogeneous distribution
- Mode of fibre failure (pull-out or fibre fracture)

3.4.4 Rheologocal and flowability tests

High pressure capillary rheometer Goettfert Rheograph 75 is used to evaluate the viscosity. Viscosity is measured according to DIN 54811 at 180, 200 and 220°C at shear rate range of 1 s^{-1} up to 1E6 s^{-1}. Twin dies with 1 mm diameter and different lengths of 0.2 and 15 mm were used to establish pressure difference.
To validate the rheological results, spirals are injection moulded according to ASTM D3123-09. Figure 3-3 shows the spiral mould with an outer diameter of 250 mm, pitch 9.5 mm and semi-circular cross-section of 6 mm diameter. The spiral has a half circular cross section. Lengths of the injection moulded spirals are measured against a printed pattern foil as shown in Figure 3-4. Also the fibre content is analysed at 100 mm step along the spiral length to check the homogeneity of fibre distribution. Fibres are extracted according to [Ram14] in order to monitor the development of fiber length and diameter along the spiral length using the different NFTC systems. The extracted fibers from each spot are then air pumped by the wet dispersing unit (Lixell) using the QICPIC machine according to ISO 13322-2. The fibres are dispersed in Isopropanol with a magnetic stirrer to ensure no water absorption by the fibres. The dispersed fibres are then pumped through a closed cycle and the fibres are photographed, as shown in Figure 3-5, with a high speed camera capable of 450 photos per second. Two types of lenses with different resolution are used namely M8 (20-6820 µm) and M6 (5-1750 µm). The images are saved and further processed to depict the fibre length (LEFI) and diameter (DEFI).

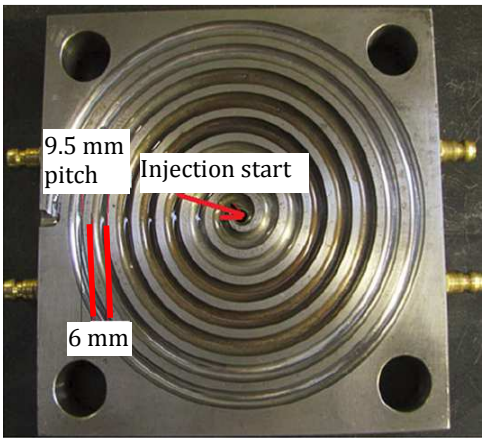


Figure 3-3: Spiral injection moulding

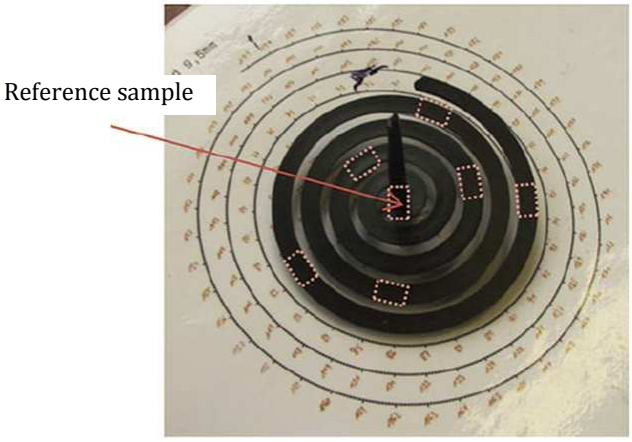


Figure 3-4: Fibre extraction positions

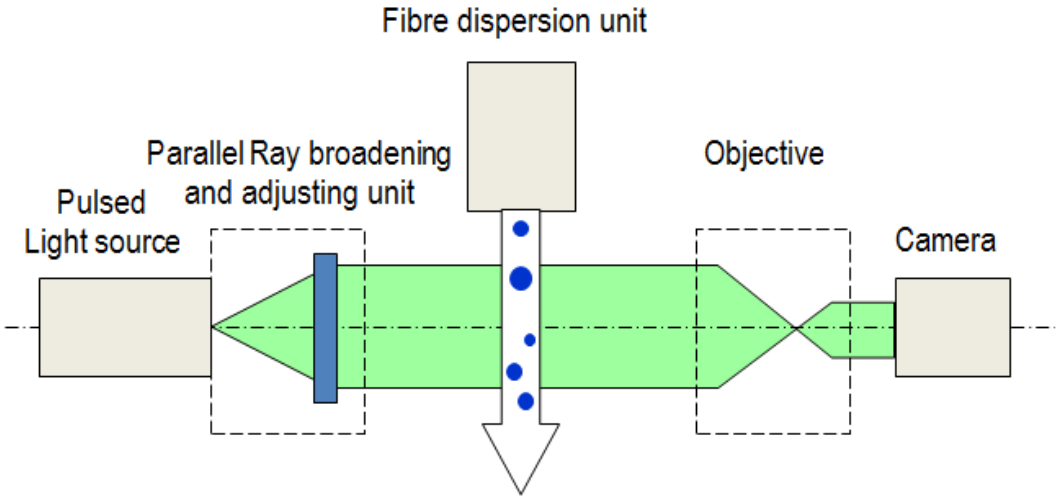


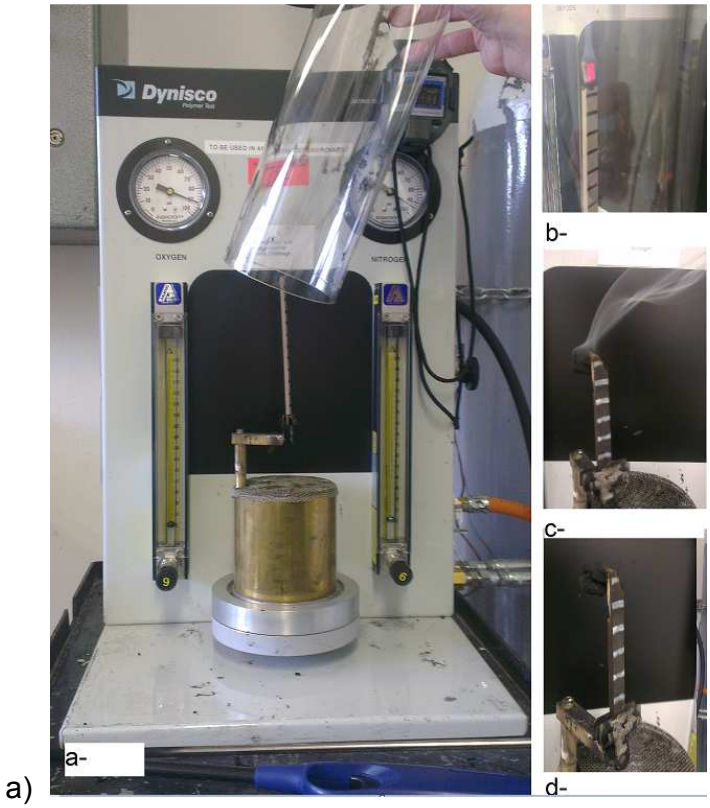
Figure 3-5: Fibre imaging concept in QICPIC (Source: Sympatec)

3.4.5 Flame retardance tests: LOI, UL94 and Cone calorimetry (DIN EN ISO 4589, DIN EN 60695 and ISO 5660-1)

Different flammability tests are carried out such as

a) LOI test: LOI test measures the required oxygen concentration required to support the flame sustainability. Samples of type A (125*6.5*3 mm^3) are injection moulded. The test is carried out using Dynisco equipment where the sample is mounted vertically as shown in Figure 3-6 a. The test proceeds as follows:
   An arbitrary initial the oxygen to nitrogen ratio is selected. Fire is applied using a flame and when the sample is well lighted remove the ignition flame. The criterion of burning for physically supporting sample type A is at least 3 minutes or 50 mm burning length. Evaluation is done according to the instructions of the equipment manufacturer based on ASTM D-2863. All the observations from the firing, smoke colour, after glow and final shape of the sample should be considered as shown in Figure 3-6 b-d.
b) UL94 test: UL94 is a test which classifies plastics according to their burn behaviour at a certain orientation and thickness. From lowest (least flame-retardant) to highest (most flame-retardant), the classifications are: NR (not rated), HB (horizontal orientation), V-2, V-1, V-0 (vertical orientations). Samples of UL94 are either injection moulded or cut directly from the press moulding samples. Dimensions of UL94 samples are 125*12.5*3 mm^3. The test is carried out according to IEC/DIN EN 60695-11-10 and -20 standards as shown in Figure 3-7. Rating range of the sample is not-rated, HB, V2, V1 and the best retardant is V0 rating.
   - V0: Burning stops within 10 seconds after direct flame exposure to the sample for ten seconds. No flaming drips are allowed
   - V1: Burning stops within 60 seconds after direct flame exposure to the sample. No flaming drips are allowed.
   - V2: Burning stops within 60 seconds after direct flame exposure to the sample. Flaming drips are allowed.
   - HB: Slow horizontal burning on a 3 mm thick specimen with a burning rate is less than 75 mm/min or stops burning before the 75 mark. HB rated materials are considered "self-extinguishing".
   - Otherwise is not-rated
c) Cone calorimeter testing: At least three samples are required with the dimensions of 100*100*3 mm3. The main values taken from the calorimetry results are: peak heat release rate (PHRR), Maximum average rate of heat emitted calculated from HRR-Time per m² (MARHE), total heat released per m² (THR), total smoke released normalised for the surface area of the specimen (TSR), time to stable ignition of at least 5 s (TTI), time to peak heat release rate (TTPHRR), time to flame distinguishing (TT flame out) and mass loss in comparison to the original value (Total mass loss).
   The cone calorimetry concept is based on the direct proportionality between the heat released by burning materials to the quantity of oxygen used in the

combustion process. This name (cone) was derived from the shape of the truncated conical heater that is used to irradiate the test specimen with fluxes up to 100 kW/m2 in the test [Law09].



a)

Figure 3-6: Concept of LOI test

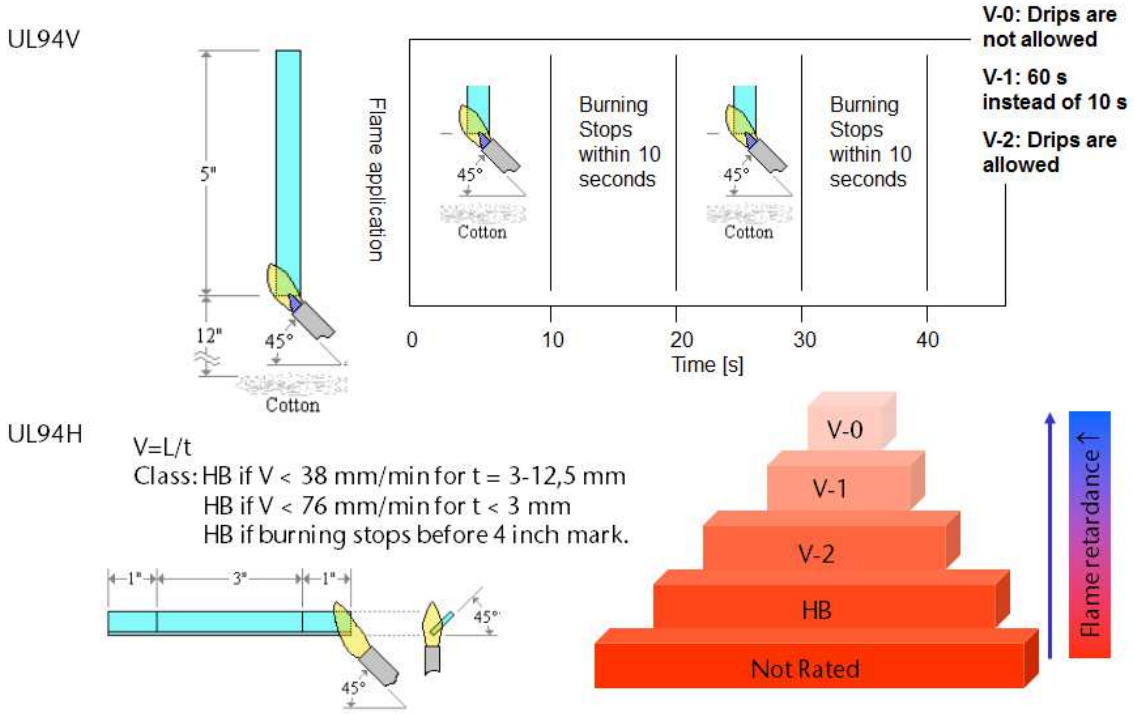


Figure 3-7: Concept of UL94 rating test

3.4.6 Water absorption test

Water absorption test is conducted also according to DIN 53495-method 3 where the weight of the sample is observed after 30 min at 100°C distilled water followed by 15 min at 23 °C in distilled water and finally drying of the sample. It is just a comparative test not till the saturation. The result of the weight (after test) is compared against the weight before test.

3.5 Statistical evaluation of results

Results are evaluated either by ranking the results with respect to every condition/ material/ method or making a combined performance ranking in case of many several considered responses; see section 4.1 where different responses of E-modulus, strength, impact and water absorption are considered for different treatment methods.

Another statistical evaluation is followed like in section 4.2 where different parameters are affecting different responses. The problem is more complicated, so the computer software ‘JMP®10.0.0’, which is developed by JMP business unit of SAS institute for analytics in USA, is used with user defined number of examples (more than recommended by the design of experiments module) and then the model is run using the least square method.

Two tailed t-test with 95% confidence is also used for checking the significance of population results as seen in section 4.2.

4 Treatment of Natural Fibres/Thermoplastics and Selection of Coupling Agents

4.1 Selection of pre-treatment/ modification/ coupling agent

4.1.1 Introduction

In order to be compared with glass fibre composites; NFTC should be characterised with high specific mechanical properties, reproducibility and acceptable physical properties such as water absorption resistance and thermal degradation. This section focuses on the flax/polypropylene composite and aims to improve its properties through different modifications either mechanically or chemically. Different chemical modifications were tried for either fibre or matrix to improve the adhesion of matrix to fibre overcoming the hydrophilic nature of the fibre [Kar97], [Arb06], [Ruk07]. Increase of fibre matrix adhesion leads to the rise of the interfacial shear strength and the decrease of the critical aspect ratio Equation 2- 5 and hence efficient load transfer is attained. The chemical modification can be achieved by modifying the hydroxyl groups present mainly in fibres' cellulose with reactions such as alkalisation, acetylation, isocyanation, coupling agent treatment and grafting. Alkalisation promotes fibrillation and rough surfaces formation which in turn increases the mechanical efficiency [Bog07], [Gra14]. As mentioned in 2.3.1 different modification methods are in the literature reported. Acetylation is useful for the sake of dimensional stability of the end-product [Arb06]. Isocyanation induces better interaction with thermoplastics [Wan04]. Coupling agents such as silane or maleated anhydride grafted polypropylene improves the fibres' wettability due to the agent's long chain and thus improves the affinity to the thermoplastic matrix as polypropylene [Bog07]. Silanation restrains fibre swelling [Li07]. Both fibre pull-out and fibre-matrix debonding are reduced [Gas97] Finally grafting of either vinyl groups or thermoplastics induced with peroxides onto the surfaces of fibres enhanced the fibre-matrix adhesion [Bog07], [Mis01].

In this work; flax fibres are first alkalinised, then modified by silanization with TMVS and acrylation using AA. These treatments help primarily in forming strong covalent bonding and thus raise the mechanical strength and stiffness [Li07]. Also water absorption is expected to decrease due to the reduced hydrophilicity of fibres resulting from the hydroxyl groups' reaction. On the other side, the PP matrix is also modified Polypropylene matrix PP is functionalized with maleic anhydride MA in acetone solution, liquid TMVS and AA. Thereby, coupling agents of MAPP, TMVS and AAPP are formed.

4.1.2 Strategy of experiments

The used materials, as mentioned in section 3.2, are: Flax fibres as natural fibre, PP of MFR 52, MA for grafting, peroxide "Luperox 101" as a catalyst, (MA, TVMS and AA) for fibre and matrix modification. More data about the material and the suppliers are found in section 3.2.3. The treatments of both flax fibres and PP matrix are shown in

Table 4-1. The reference composite sample will be made of non-treated fibre as well as non-treated PP matrix. Otherwise, there are three fibre treatments for the flax fibres namely (alkalinisation with NaOH, NaOH +TMVS, NaOH + AA) or on the other side, PP is treated with three grafting methods namely MAPP, a mix of TMVS and MAPP and AAPP.

The composite made out of these treatments are named according to fibre treatment / Matrix treatment; i.e. NaOH/MAPP as an example. Each treatment will be tried at a reference level of 30 wt-% flax content. But only five combinations of treatments (--/--, NaOH/MAPP, NaOH/TMVS-MAPP, NaOH-TMVS/MAPP, NaOH-TMVS/TMVS-MAPP) are tried with the varying flax content of 0-50 wt-%.

Alkalinisation step of fibres is conducted firstly to clean the fibres from surface contaminants. Fibre bundles are washed with 2% sodium hydroxide solution for 1 hour to remove possible impurities. The fibres are washed with water then with acetone. Fibres are then left to dry at 80°C for 48 hours.

After being alkalinised; the process of fibre treatment by TMVS and AA takes place before the drying step using 10% solution for almost 5 minutes prior to washing. Microscopic investigation using SEM tests is applied to investigate the fibre adhesion to matrix. Infrared analysis FTIR is carried out on the treated fibres using Stepscan-FTIR-Spektrometer FTS 7000 over a wave number range of 4000 – 400 cm^{-1}.

Table 4-1. Plan of experiments for fibre and matrix

Matrix of fibre/ matrix treatment		Flax fibre treatment			
		No treatment	NaOH	NaOH-TMVS	NaOH-AA
PP matrix treatment	No treatment	0-50 wt%			
	MAPP		0-50 wt%	0-50 wt%	30 wt%
	TMVS-MAPP		0-50 wt%	0-50 wt%	30 wt%
	AAPP		30 wt%	30 wt%	30 wt%

Preparation of the compatibiliser MAPP: PP is mixed with maleic anhydride in a weight ratio of 98:2, prior to the addition of 1% of the peroxide catalyst. This mixture is extruded at 180°C and 200 rpm. Then, the resultant is mixed mechanically with PP at 5 wt%. The approach of modifying matrix with a constant amount of copolymer is to investigate the possibility of producing a standard polymeric matrix that can be further mixed with the reinforcing fibres. Also it is aimed to prevent excessive polymer crystallisation to be hardly processable.

Silanation by TMVS: Trimethoxyvinylsilan is mixed with MA, dissolved in acetone, peroxide and PP with the ratio of 4.5:4.5:1:90. This mixture is extruded and blended

with PP in a 5: 95 ratio. Finally Acrylation takes place by mixing acrylic acid with PP in 3:97 PP, then extruded together at 180°C and 260 rpm. Afterwards, the mixture is mixed mechanically with PP in ratio of 5:95.

Melting point is determined by DSC to characterise the resulting coupling agent whether it is compatible with the host polymer in further processing. Degree of crystallinity is calculated taking the perfect 100% crystalline PP as 207 J/g

The compounding process of flax with PP takes place in Berstorff ZE25 twin co-rotating extruder. Fibres are drawn as a sliver. The flax fibres weigh 20 g/m in average. The modified matrix is fed, as explained in [El-14c], to get the required weight fraction which ranges between 10 to 50% in steps of 10. Temperature pattern in the extruder is chosen to keep 200°C at the entrance of the fibres and ends with 180° at the outlet. Screw elements are selected with low shearing load to avoid excessive fibre damage (low number of kneading elements). After cooling, the resulting compound was shredded using mechanical shearer. Injection moulding of mechanical samples, samples adaptation, water absorption and mechanical testing are all conducted as described in 3.4.1. SEM is then applied on the sample fracture surface to investigate the failure mode corresponding to the different chemical modifications.

4.1.3 Effect of fibre treatment

Photographs of flax fibres before and after treatment obtained by SEM are shown in Figure 4-1. Impurities are easily observed on the surfaces of the raw flax fibres in Figure 4-1 a. Alkalisation process helps in removing these impurities as in Figure 4-1 b. Fibres treated with TMVS exhibit slightly a polymer adhesion at the surface as shown in Figure 4-1 c. AA treatment has also gained the same surface feature with a greater scale as shown in Figure 4-1 d. Even at higher magnification in fig. 1e, the surface seems to be fibrillated as there are continuous parallel lines along the technical fibre direction. Figure 4-2 shows the FTIR analysis of the four fibres. Table 4-2 presents the main changes in peak positions corresponding to the vibration groups. The peak at 3350 cm^{-1} corresponds to the free hydroxyl group [Sha03]. Increased intensity of this peak is observed through sodium hydroxide washing. This is attributed to the cleavage of the alkali sensitive bonds [Ray01] and the breaking of the hydrogen bonding in cellulosic O-H groups [Tah07b], [Tse05]. However, other treatment with AA shows lower intensities at this peak. AA is likely to homopolymerise rather than to react with fibre [Li03].

The effect of removing pictins and fats can be observed at the peak of 1732 cm^{-1} which corresponds to C=O stretching vibration suggests the existence of carboxylic/ester groups. After alkalinisation, the 1732 cm^{-1} peak is still present indicating the presence of pictins. This peak is reduced after TMVS and AA treatments.

Lignin presence is detected by the shoulder at 1450 cm^{-1} band, peak at 1050 cm^{-1}, 887 cm^{-1} and 817 cm^{-1}. Another change is observed at the diminishing of the C=C vibration group at 1516 cm^{-1} by removing instauration in oil traces and fatty substances [Mwa99].

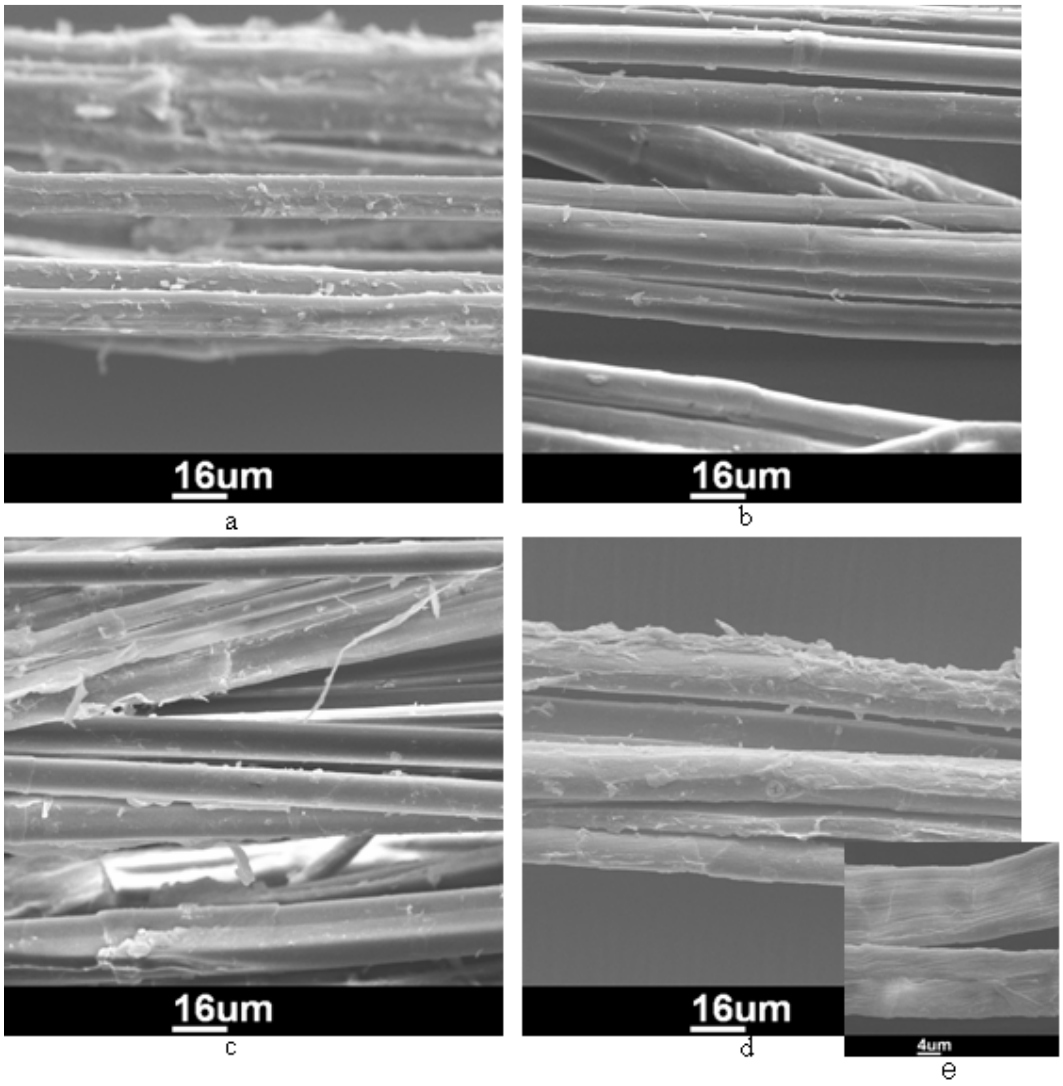


Figure 4-1: Effect of treatment on flax fibre surface: a-not treated b-NaOH c- NaOH+TMVS d-NaOH+AA

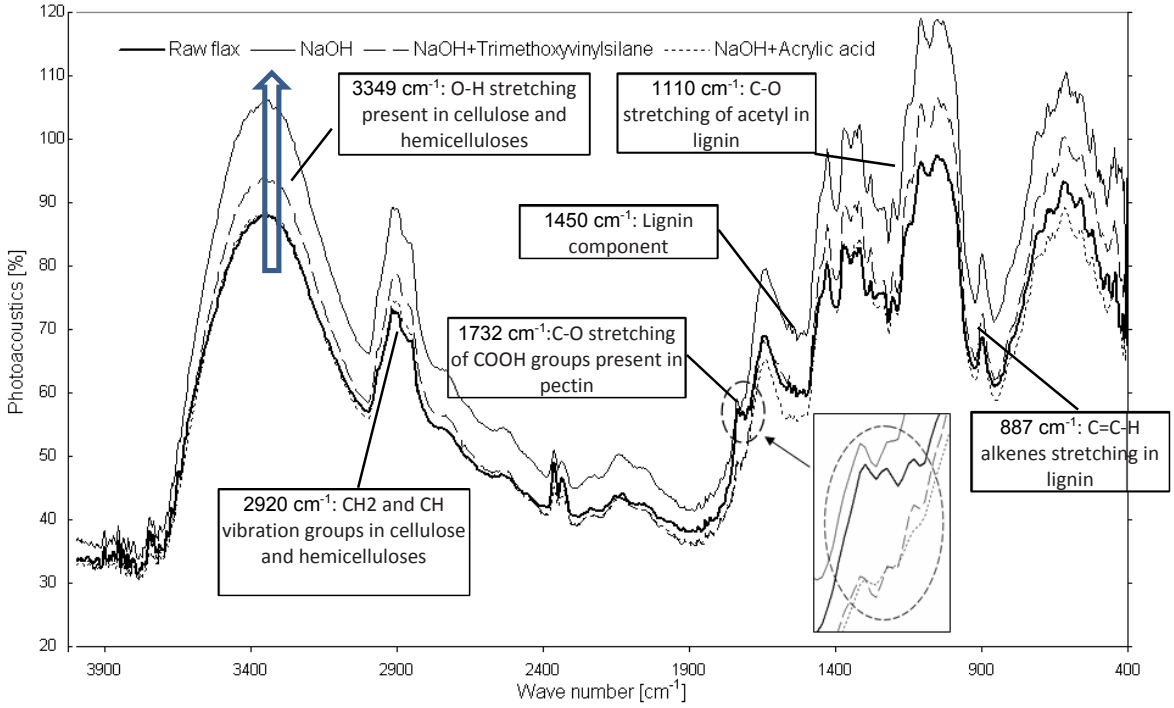
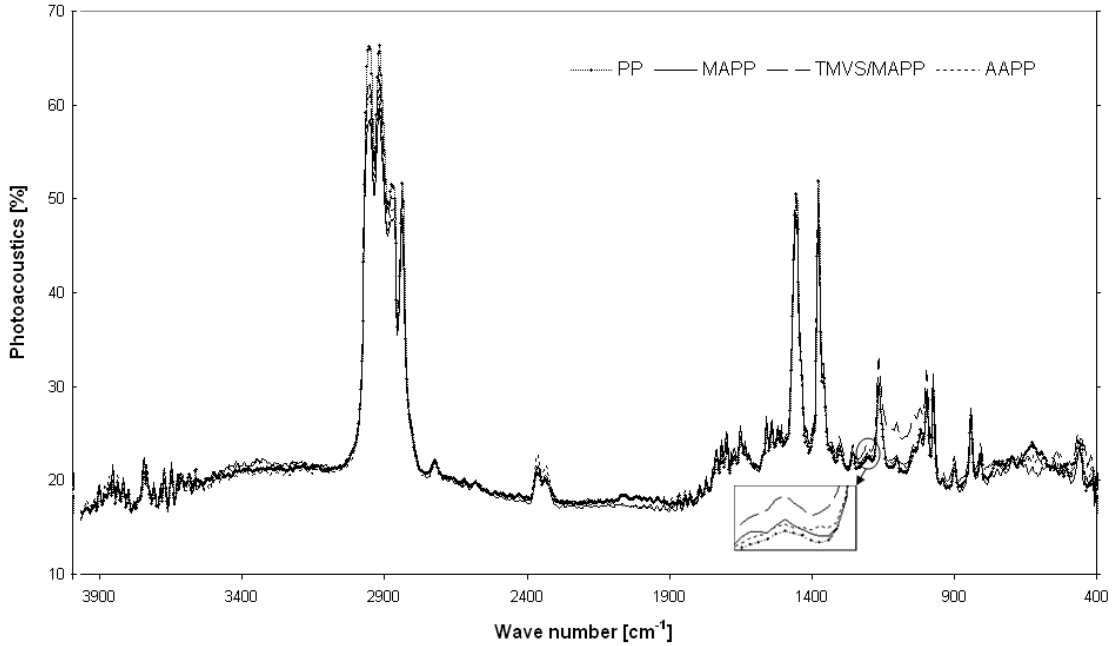


Figure 4-2: FTIR of the flax treated fibres and the main peaks

Table 4-2. FTIR spectral data of raw and treated flax

Photo-acoustic absorption band [cm^{-1}] of flax with the following treatment				Notes
--	NaOH	NaOH/ TMVS	NaOH/ AA	
3349	3349	3349	3350	O-H stretching present in cellulose and hemicelluloses
2920	2916	2912	2916	CH2 and Ch vibration groups in cellulose and hemicelluloses
2847	2866	2873	2870	CH2 and Ch vibration groups in waxes and fats
1732	1736	1736	1732	C=O stretching of COOH groups present in pectin
1636	1637	1636	1637	Asymmetrical oscillation of ionised carboxyl groups in pectin
1508	1516	1516	1516	C=C stretching vibration
1450	1454	1458	1454	Lignin component
1429	1428	1428	1428	Symmetrical oscillation of ionised carboxyl groups in pectin
1373	1373	1373	1373	C-H bending
1342	1338	1338	1338	O-H bending
1053-1110	1060-1110	1056-1110	1056-1110	C-O stretching of acetyl in lignin
887-817	902-813	989-813	894-810	C=C-H Alkenes stretching in lignin

4.1.4 Effect of matrix treatment



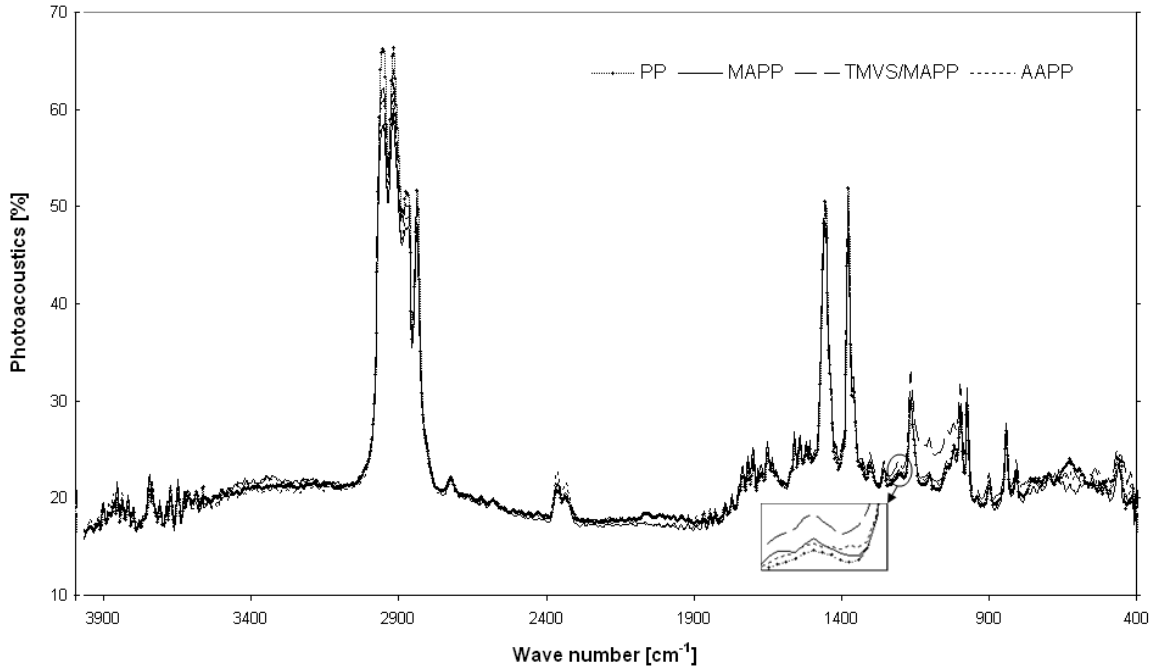


Figure **4-3** shows the FTIR analysis of the homopolymer PP and its modifications. No major modifications are observed except at the band region at 1207cm^{-1} due to the methyl groups of TMVS [Shi07]. This provides evidence for the incorporation of the silane compounds into the PP. The peak at 1207 cm^{-1} in the spectrum of the silanated PP corresponds to the CH_3 rocking vibration of the methoxysilane groups (Si-O-CH_3) of the VS and MS grafted onto the PP backbone. DSC results are presented in Table

4-3. It shows an approximately equal increase of the crystallinity. This indicates the expected rise of the mechanical properties as reported by Arbelaiz [Arb06].

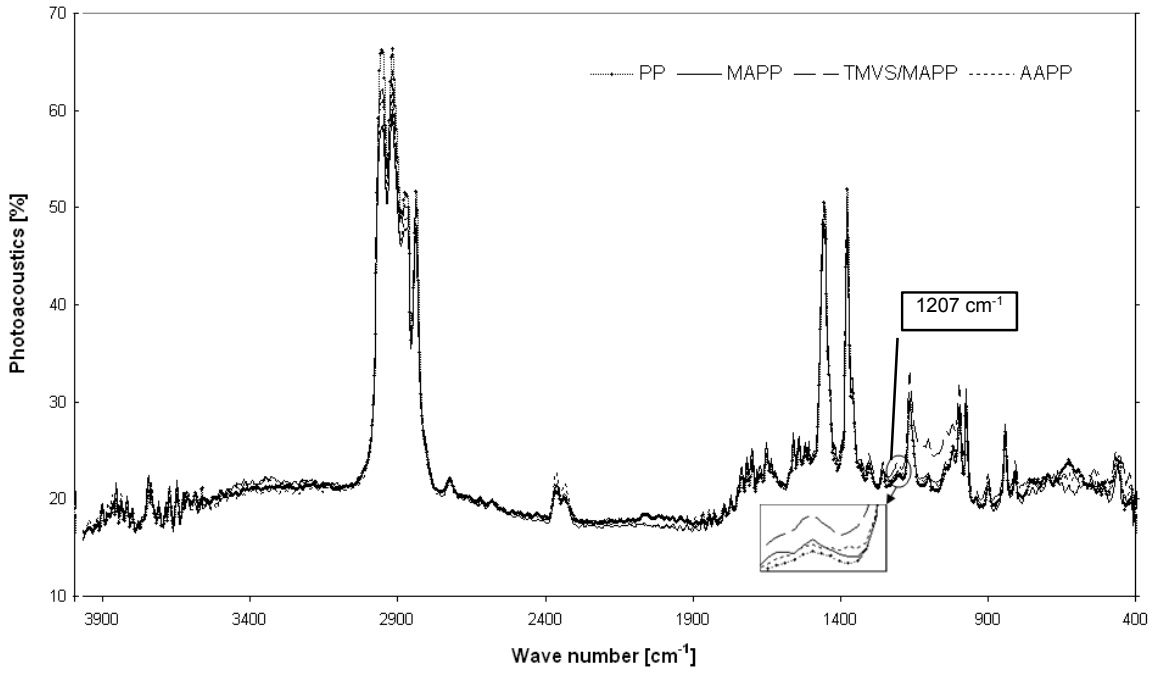


Figure 4-3: FTIR of the modified PP matrices

Table 4-3. DSC results of the treated matrices

	PP	MAPP	TMVS	AAPP
Melting point [°C]	172	164,8	164,6	164,9
Crystallinity [%]	29,30	37,90	37,10	37,97

4.1.5 Effect of the treatment at different fibre content

As shown in Table 4-1, only five treatments (including the untreated case) are applied on the whole spectrum of fibre content [0-50 wt-%].

Figure 4-4a shows the effect of the fibre content on the composite E-modulus. The main effects of fibre type and fibre/matrix treatment on E-modulus, tensile strength, unnotched Charpy impact strength and water absorption are shown in Table 4-4

Table 4-4. Effect of fibre content and fibre/matrix treatment on the composite properties

	Investigated variable			
Effect of:	E-modulus	Tensile strength	Unnotched Impact strength	Water absorption
Fibre content	• A linear trend improvement* in E-modulus compared to the untreated composite till almost 50%**. • For instance the improvement at 40 wt% is almost 181-300% for the different treatments. This is more than 150% improvement reported by [Tah07b].	• In contrary to E-modulus; strength does not show linear improvement with the increase of fibre content as shown in Figure 4-4b. • Maximum strengths are attained at 30 wt% with 176-210% improvement, and then more fibre content causes a drop of the recorded results***.	• By increasing fibre content, impact values decrease from 35-42 kJ/m² to 8-10 kJ/m² abruptly at 10% fibre. After that, a persistent decreasing trend is followed.	• The increase of fibre content leads to an increase in water absorption. This is activated by diffusion exploiting the micro-gaps, compounding micro-cracks in matrix or the incomplete wettability positions between fibres and matrix [Pan07].
Treatment	• All treatments show an increase in E-modulus of the un-reinforced matrices as an evidence of the increase of the polymer crystallinity	• MA matrix treatment exhibits best tensile strength results while TMVS appears to give some softening for the matrix which can be assured by the corresponding E-modulus values in Figure 4-4a.	• There is a superiority for NaOH/MAPP and NaOH-TMVS/MAPP • In general, Regardless treatment type, the impact value decrease.	• Both silanated and MAPP samples exhibit an improvement in resisting water absorption.

* Improvement trends are linear until 40 wt% where 8-9 GPa values are reached. NaOH/ MAPP and NaOH-TMVS/ TMVS-MAPP treatments exhibit slightly better results than those of NaOH/ TMVS-MAPP and NaOH-TMVS/ MAPP.

** A drop in E-modulus is observed at 50 wt%. This can be attributed to the improper selection of screw elements and hence poor fibre distribution is found at higher fibre content.

*** The strength results for extruded flax/PP with MAPP/NaOH system reached 58.7 MPa. It is reported in [Bos02] that extruded compound of Flax/PP/MaPP at 50 wt% reached almost similar values. In other words the results of this work show faster improvement till 30 wt% compared with [Bos02]. At higher fibre wt% the literature results continues its improvement in contrary to the work results which dropped

to lower strengths. This remark can be attributed to two factors. Firstly the un-successive mixing conditions at higher wt%, and the second is that the copolymer was not sufficient to react completely with the fibres regardless they are treated or not. Copolymer amount should be optimised as shown later in section 4.2

**** Up till 40% MAPP samples show better behaviour. Water absorption decrease is attributed to the reaction with the free hydroxyl group and to the reduction of the voids between the fibre and the matrix as an indication of better adhesion [Dem06]. This may explain the better behaviour of MAPP samples shown in Figure 4-4d.

According to [El-09b] pull-out failure mechanism dominates the fracture area when the fibre content is less than a critical value. Otherwise features of fibre or matrix fracture characterise the sample fracture. Figure 4-5 shows SEM photographs of the fracture surface areas for samples of different fibre content. It should be noted for all samples that the fibres' lateral surfaces are coated with polymer surface due to the success of MAPP as a coupling agent. The fibres are more or less difficult to be differentiated regardless the fibre content. This indicates that the fibres are not pulled out alone but they are well adhered with the host matrix. Also it is inferred from Figure 4-5a where fibre content is 10% that the pulled out fibres' terminals are also coated with polymer. This is an evidence of fibre pull out without fibre fracture. In contrary; Figure 4-5b shows clear fibre fracture at 20 wt% in many fibres. Figure 4-5c shows the more fibre fracture features at 40 wt%. Figure 4-5d shows a zoom-in for one of these fibres. Debonding between fibre and matrix where the force direction is in orthogonal direction to the fibre length is illustrated in Figure 4-5e. Finally another observation is highlighted that even with high fibre content the fibres are well distributed without agglomeration features. This is also reported previously by Arbelaiz [Arb05] about the role of MAPP as dispersing agent between polar fibres and non-polar matrix. This is attributed to the lowering of the surface energy of the flax fibres to be close to that of the matrix. Thus results in the good wettability of PP onto the surfaces of the flax fibres' surfaces.

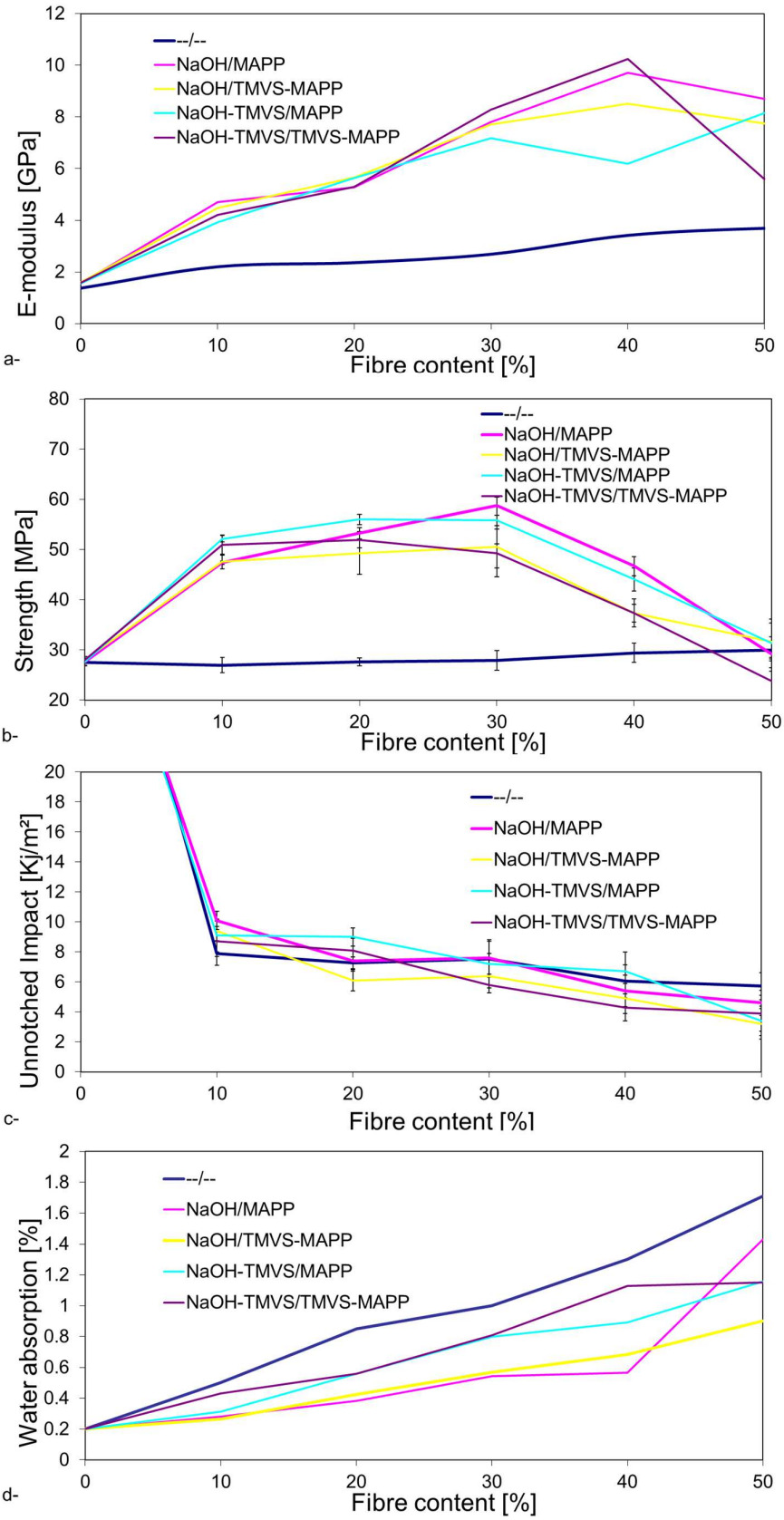


Figure 4-4: Effect of chemical treatment on a- E-modulus b- Strength c- Impact d- Water absorption

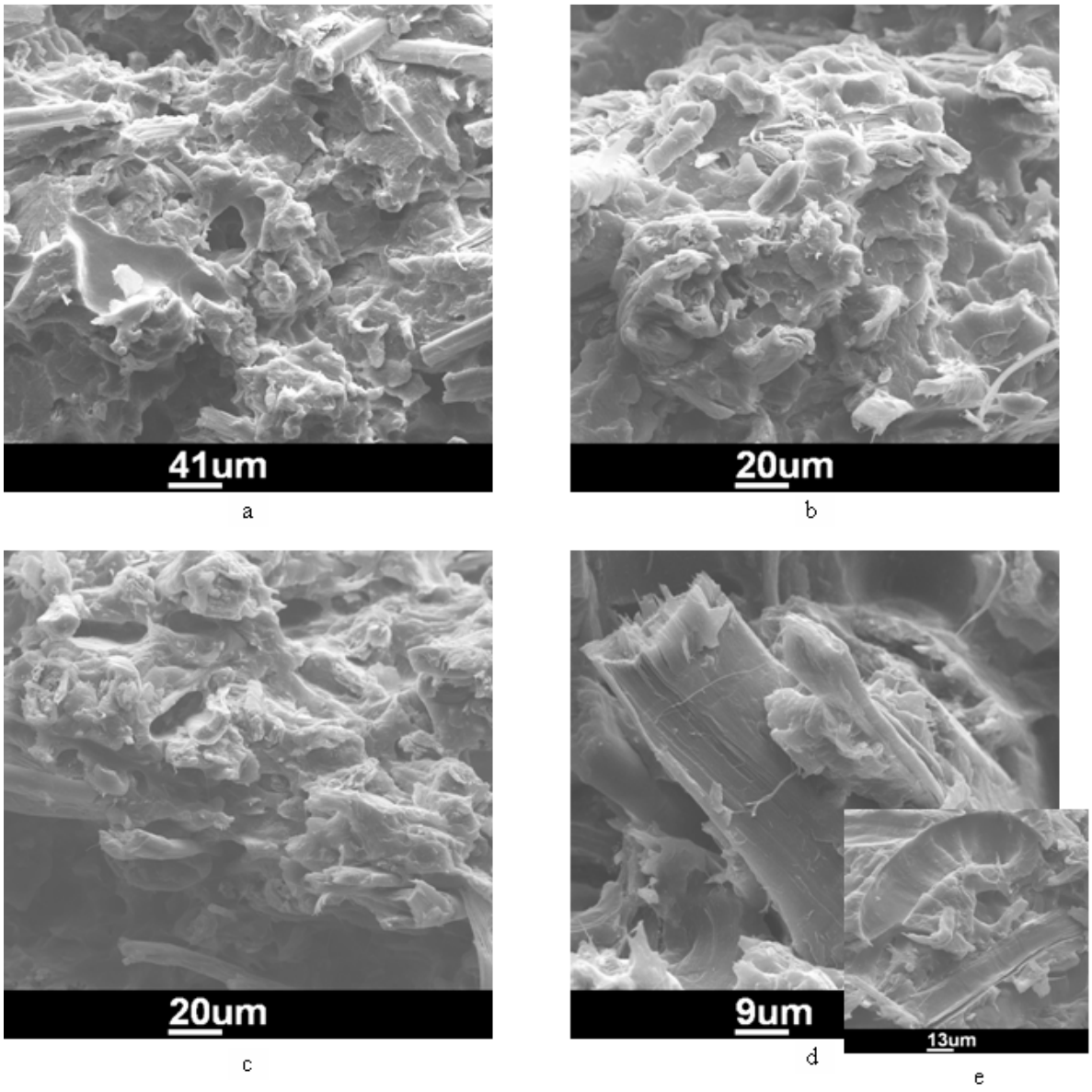


Figure 4-5: SEM of impact specimens of NaOH-flax/MAPP-PP system a- 10%, b- 20% c,d,e- 40%

4.1.6 Effect of the fibre/matrix treatments (nine combinations) at 30 wt%

Figure 4-6 shows both the mechanical and water absorption results attained with different modifications of the fibre/matrix system at flax yield of 30 wt%. Considering matrix modification; AAPP show better results for E-modulus while MAPP have better performance in impact and water absorption. It is difficult to detect significant difference between matrix treatments on the tensile strength.

Considering fibre surface modification; TMVS was distinguished for E-modulus and strength where only sodium hydroxide washing was enough for impact and water absorption. From Figure 4-6; it can be inferred that the matrix treatment plays more important role than fibre treatment. Arbelaiz [Arb05] reported also that matrix is more influenced than fibres by TMVS treatment. MAPP presence seems to be very effective

in resisting water absorption regardless the presence of TMVS as it reaches one third of the untreated flax/PP water absorption value. While AA presence or its functionalized groups shows the worst influence on the composite water absorption.

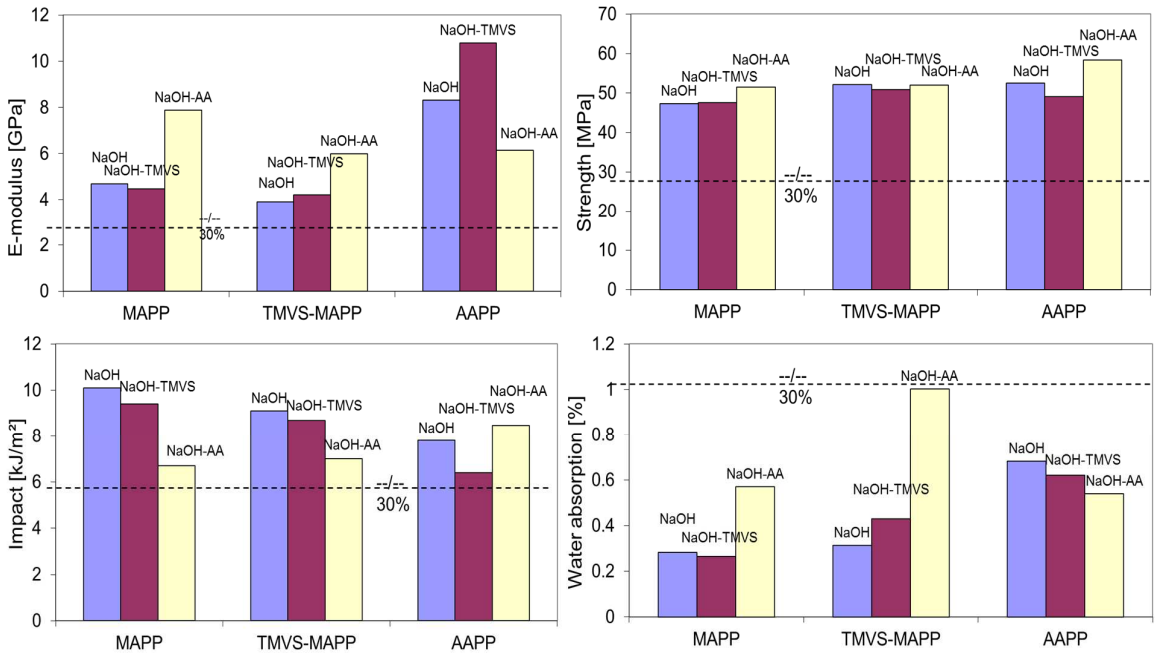


Figure 4-6: Effect of different fibre/matrix treatment on the mechanical properties and water absorption at 30 wt% fibre content

Regardless of the low impact values for the treated fibre/matrix systems at 30 wt% but SEM photographs illustrate some interesting observations.

a- NaOH/MAPP: The highest impact toughness value achieved by MAPP/NaOH is justified by the fibre with an adhering matrix as shown in Figure 4-7a. Crystalline fracture features are also remarked. Each fibre retains its integrity without further fibrillation.

b- NaOH-AA/MAPP: Figure 4-7b shows low impact value attained by MAPP/NaOH-AA. This is is justified by the pulled-out fibres. It is obvious that the fibres are coated with a layer indicating successful function of the copolymer agent. However, there are fibrillation features indicating weakened fibre inter-lamellar shear strength by the effect of AA.

c- NaOH/TMVS-MAPP: Figure 4-7c has similar features of fibre matrix adhesion and fibre fracture compared to that of Figure **4-7**a. The only difference lies in the presence of an additional fracture mode which is the debonding of the fibre lateral surface. This explains the relatively weaker impact.

d- NaOH/AAPP: Figure 4-7d highlights that the fibres are not homogeneously distributed in the matrix modified by the AAPP copolymer agent. As there are some fibres which are good immersed in the matrix and others which are agglomerating. So many fibres are pulled out easily without a reaction layer on their surfaces. Although these observations of low qauality dispersion; the fibres

retain their integrity and no signs of fibrillation are exhibited. Also the crystallinity of the matrix is obvious. These two factors can explain the good E-modulus value attained by this system where as its impact toughness value is low. Another two factors can explain the low attained impact values. First is the poor distribution of the fibres which is attributed to the lack of dispersion ability by AAPP. Second is the lack of compatibility between fibres with the AAPP modified matrix. These two factors are also remarkable using the same AAPP matrix modification with different fibre modification.

e- NaOH-TMVS/AAPP: Fibres agglomeration and deficiency of reaction layers between the fibre and the matrix are also noted in Figure 4-7e.

f- NaOH-AA/AAPP: a comparably better behaviour is shown in Figure **4-7**f for the AA modified fibres due to the compatibility between the fibre and the matrix where both of them are modified with AA. The polymeric feature of the fibre's surface is clearly an evidence of fibre matrix bonding.

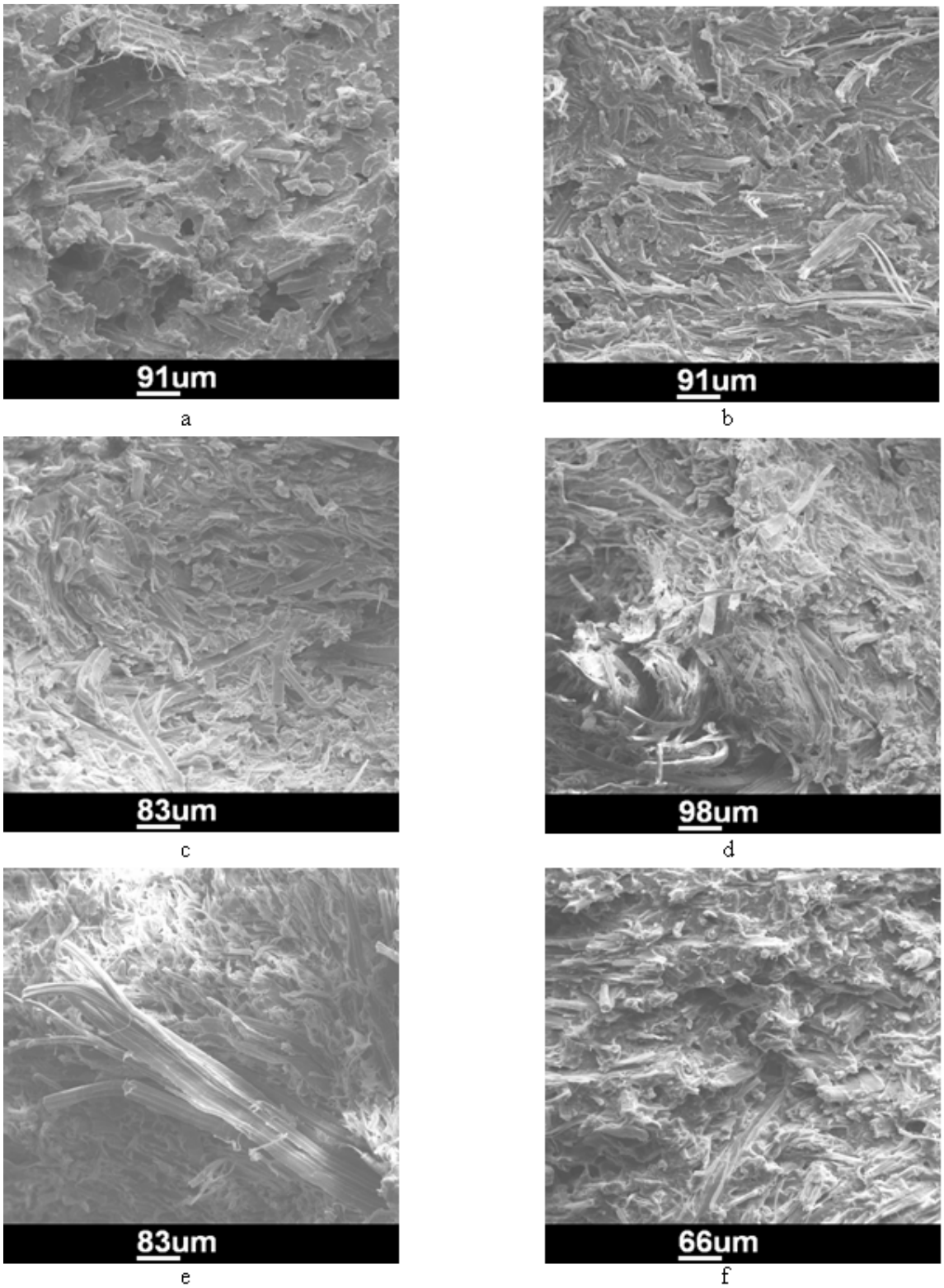


Figure 4-7: SEM photographs of fracture impact specimens with matrix/fibre treatment of: a- NaOH /MAPP b- NaOH-AA/MAPP c-NaOH/TMVS-MAPP d- NaOH/AAPP e- NaOH-TMVS/AAPP f- NaOH-AA/AAPP

4.1.7 General analysis of the results

The results of the different fibre/matrix treatments should be analysed with respect to the results gained in E-modulus, strength and un-notched impact strength. The results are normalised regarding the maximum value in percentage. Water absorption results are related to the minimum value which represents the best result in reciprocal form. Table 4-5 lists the used results in the normalising process. An average performance index is calculated, as shown in Equation 4-1, by finding the average value of the normalised values of the four measured properties. As shown in Figure 4-8, the NaOH/MAPP has relatively the best results.

Of course, this result assumes that the four considered factors have equal weights of importance. However this study is limited to these factors. Another reason encourages us to be satisfied with this treatment combination (NaOH/MAPP) which is the availability of the system and its fair cost to be implemented without too much pre-processing. That is why the next sections will follow this treatment as a reference for further studies.

$$Index = \frac{1}{4}\left(\frac{E-\mathrm{mod}\,ulus}{E-\mathrm{mod}\,ulus_{\max}} + \frac{Strength}{Strength_{\max}} + \frac{\mathrm{Im}\,pact}{\mathrm{Im}\,pact_{\max}} + \left(\frac{Absorption}{Absorption_{\min}}\right)^{-1} \right) x100$$

Equation 4-1

Table 4-5. Effect of treatments on mechanical results and water absorption at 30 wt-% flax

Fibre treatment	Matrix treatment	E-modulus [MPa]	Strength [MPa]	Impact strength [KJ/m²]	Water absorption [%]
NaOH	MAPP	4701.5	47.38	**10.1**	0.281
NaOH-TMVS	MAPP	3920	52.16	9.1	0.314
NaOH-AA	MAPP	8326	52.6	7.8	0.682
NaOH	TMVS-MAPP	4475	47.624	9.4	**0.265**
NaOH-TMVS	TMVS-MAPP	4209	50.887	8.7	0.429
NaOH-AA	TMVS-MAPP	**10793**	49.07	6.4	0.621
NaOH	AAPP	7883	51.48	6.7	0.571
NaOH-TMVS	AAPP	6000	52.00	7.0	1.004
NaOH-AA	AAPP	6154	**58.38**	8,4	0.538
		10793 (Max)	58.38 (Max)	10.1 (Max)	0.265 (Min)

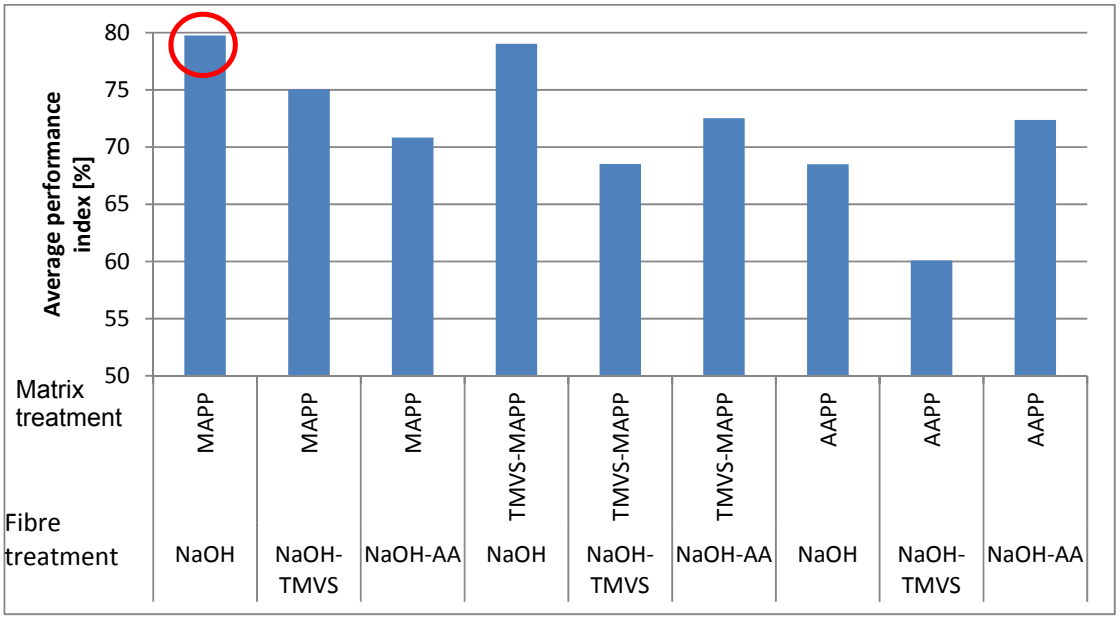


Figure 4-8: Effect of different fibre/matrix treatments on mechanical properties and water absorption

4.1.8 Outcomes

MAPP proves its ability to disperse the fibres and thereby better homogeneous material is attained. Increase of fibre content improves the E-modulus linearly until 40 wt%. MAPP/NaOH and TMVS-MAPP/NaOH-TMVS show 285 and 300% increase in E-modulus at 40 wt% respectively. Strength increased with the addition of fibres till 30%. MAPP/NaOH system improved the strength by 210%. Drop of the strength at higher percent is related to inadequate extrusion conditions.

The 5% MAPP modification is better than the other modifications in general and specifically in impact and water absorption. It is difficult to detect significant difference between matrix treatments on the tensile strength. Considering fibre surface modification; TMVS was distinguished for E-modulus and strength whereas the sodium hydroxide washing was enough considering impact and water absorption. Washing of fibres with sodium hydroxide 2% for 24 hours was able to get rid of the impurities from the fibres' surfaces. But chemical treatment of fibres does not show a big significance considering the mechanical properties in comparison with the matrix treatment.

The most important outcome of this section is defining the treatment combination which will be followed in the next investigation sections. This treatment is the alkalinisation of fibres with NaOH and the use of MAPP to induce the coupling between the cleaned surfaces of the defibrilled flax and the PP matrix.

However, how the parameters of alkalinisation as well as MAPP use in NFTC should be optimised. This is the topic of the next section

4.2 Investigation of the selected treatment for improved performance

4.2.1 Introduction

Of the previous experiments in section 4.1, alkalisation and chemical grafting using MA treatment are most efficient. Alkalisation is even considered a standard step to increase the efficiency of any further treatment. MA grafting is not only used to modify fibre surface but also the thermoplastic matrix to achieve better interfacial bonding and mechanical properties in composites. It exploits the hydroxyl groups which are abundantly available in the cellulosic natural fibre from one side and grafts to the matrix polymer from the second side. Additionally, unlike acrylic acid, MA does not react with itself under typical industrial grafting conditions. MA grafting improves the mechanical properties, water absorption resistance and dimensional stability of the composites. Besides, it is suitable to be used cost-wise. Also, grafted MA, like maleic anhydride grafted polypropylene MAPP, can be used directly with the available compounding machine without inserting a new processing step to the production cycle.

An issue, however, arises during the use of the MA copolymers like MAPP. It is the presence of many rules to follow to get best results of grafting as listed in Table 4-6. Bos [Bos04] reported that 3.5% of MAPP powder (Hostaprime HC5) is optimum in kneaded PP/Flax. Keener et al. [Kee04] similarly said that 3% is optimum with MAPP Epolene for extruded PP/Agrofibre. Sain et al. [Sai04] found that 2.5% of E43 MAPP is the optimum percent in kneading PP/Wood fibre. Arbelaiz [Arb05] (5) stated that E43 MAPP should be dependent on the retted flax fibre amount in 1:20 ratio. Zampaloni et al. [Zam07] used compression moulding for PP/Kenaf fibres and reported that 3% MAPP Epolene wax G-3015 is optimum. Bos again in 2006 reported that 1:10 of MAPP (Epolene TM G-3015) to flax is optimum by kneading with PP. Pimenta et al. [Pim08] found that 6% of MAPP G-3015 is needed in the extrusion of PP/Sisal. As seen, the amount of MAPP changes from 2.5–6.0% regardless the natural fibre content. The fibre type may have an effect on the optimum MAPP% due to the cellulose content. The ratio of the copolymer to natural fibre is another suggested method to define the amount of the required copolymer [Arb05], [Bos06] regardless of the fibre type or the MAPP properties. A study is required to see the effect of different parameters and find out the range of optimal processing parameters for using the coupling agent. MAPP is taken as the studied copolymer for different natural fibres with polypropylene PP matrix. To compare with the literature results regarding the effect of MAPP effect, weight ratios are used because MAPP is not evaluated in volume fraction.

Table 4-6. Review of the different rules followed by the use of MAPP in literature

Reference	System	MA grafting	Coupling agent [wt.%]	Notes
2004, H. Bos [Bos04]	PP/Flax PP: Retiflex Flax: Belinka	MAPP powder Hostaprime HC5, Hoechst Benelux Industrie Amsterdam)	3,5%	Kneading

2004, T. Keener [Kee04]	PP/Agrofibre	MAPP Epolene	3%	Extrusion. + Study of: Molecular wt. ↓ Acid number ↑
2004 M. Sain [Sai04]	PP/Wood fibre	MAPP E-43	2.5%	Kinetic mixer at 3200 rpm, 23 m/s and 185°C. (+ flammability tests)
2005, Arbelaiz et al. [Arb06]	PP/ Flax PP: Eltex-P HV200' Flax: obtained by biological retting. some waxes and pectins were removed. Finflax	Epolene E-43, Eastman Chemical	MAPP:Flax = 1:20	Kneading
2007, Zampaloni et al [Zam07]	PP/Kenaf	MAPP Epolene wax G-3015 Eastman chemical Company.	3%	Compression moulding
2006, H.L. Bos et al.[Bos06]	PP/Flax	Epolene TM G-3015	MAPP:Flax = 1:10	Kneading
2008, M.B. Pimenta [Pim08]	PP/Sisal	MAPP G-3015	6%	Extrusion

4.2.2 Experimental plan to find the optimum use of the selected treatment

Table 4-7 illustrates the factors investigated to optimise the combined treatment namely the alkalinisation as well as the MAPP. A set of preliminary experiments (A1 and A2) is added to the plan of tests in order to find out the optimum NaOH concentration and time of pre-treatment. Then the second set (B1-B4) deals with the MAPP optimisation. The investigated factors considering the MAPP are the copolymer to natural fibre weight ratio, hereafter called MAPP:NF, the copolymer molecular weight or graft%, natural fibre content and type. Fibre content is investigated to be not limited to flax fibres. Three types of fibres are selected due to their common use. Bast fibres represented in flax and hemp. Leaf fibres which are characterised with its coarseness and relatively high E-modulus are also represented in sisal. Fibres were supplied as mentioned in 3.2.3.

Table 4-7. Plan of investigated parameters

#	Parameter	Variation
A1	NaOh conc. pretreatment	0%, 5%, 10%
A2	NaOh time pretreatment	0-24 hr
B1	MAPP : NF	0%, 6.7%, 10.0%, 13.3%, 16.7%*

B2	MAPP Source	Type A from Sigma Aldrich Type B from Kometra
B3	Fibre Content %	30%, 50%
B4	Fibre type	Flax, Hemp, Sisal

* MAPP% in 30 wt.% fibre is [0, 6.7, 10, 13.3, 16.7%] X 30% = 0, 2, 3, 4, 5%.
In 50 wt.% fibre, it is [0, 6.7, 10, 13.3, 16.7%] X 50% = 0, 3.3, 5.0, 6.7, 8.3%

Fibres are washed with different concentrations of sodium hydroxide solution for different times at room temperature to remove possible surface impurities. The fibres are washed with water then with acetone to reach neutralisation. Fibres are then left to dry at 90°C for 24 h then left in open air for 3–4 days. Before compounding these alkalinised fibres with PP, they are re-dried again at 90 °C. Two levels only of fibre contents are selected for this plan, due to their wide market application, namely 30 and 50%.

The source and the form of the coupling agent are also considered due to the effect of molecular weight, acid number, outer surface area and the probable sites of reaction and grafting [Kee04], [Kim07]. Kim [Kim07] reported that neither low nor high molecular weight copolymers help in the proper entanglement between MAPP and PP matrix. Also neither low nor high MA grafting provide balanced interaction with PP and the fibres. Molecular weight affects the resulting composite's mechanical properties in a direct proportion way [Kim07]. Two types are studied. Type A is the granulate form MAPP from Sigma Aldrich with molecular weight of 9100 g/mol. Type B is powder form MAPP supplied by Kometra (SCONA TPPP 8112) with molecular weight of 119850 g/mol. Grafting increases with MA content [Gue04]. From another side; higher molecular weight MAPP has normally lower acid number and hence lower MA content. This results in a higher melt flow index MFI, better mixing, and better diffusion [Gue04]. Therefore, both types of MAPP are studied to see the effect of different shapes and molecular weights of the coupling agent.

Compounding mechanism is carried out in the batch kneader Haake with roller type. Speed of 100 rpm for 10 minutes at 190°C is used. PP and MAPP are added firstly. Torque is observed to ensure total melting of PP and MAPP. Then the natural fibres are added. The kneaded material is then shredded. The granules are then injection-moulded into the required test samples.

4.2.3 Effect of Pre-treatment Course

Figure **4-9**a shows the effect of alkalinisation time and concentration of NaOH on the natural fibre weight (represented in trend lines). Loss in weight is taken as an indication for the removal of impurities, waxes, hemicelluloses and delignification. Logarithmic plateau form can be depicted from both curves. 24 h treatment is taken as an appropriate treatment period. Actually starting from 5 h, the weight loss in Figure 4-9b seems to be enough and the increase in loss is not so significant. The weight loss in Figure 4-9b points out that 2% is significant in comparison with no treatment. However,

5% treatment shows a good improvement even in comparison with 2%. The change from 5% to 10% cannot be considered insignificant. Therefore fibres' treatments with 0, 5 and 10% concentration values are carried out and then compounded into composites to investigate the final mechanical properties.

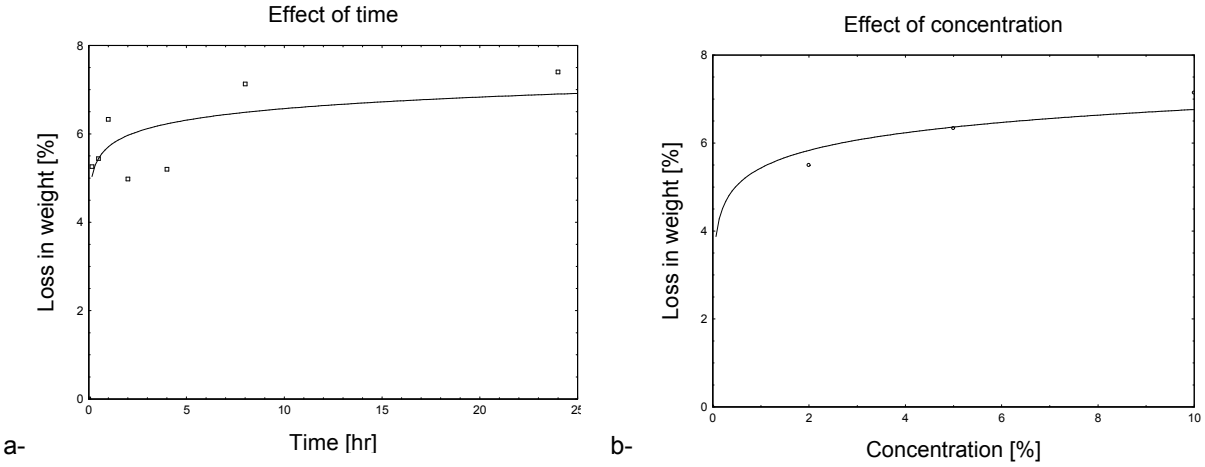


Figure 4-9: Effect of a- Time b- NaOH Concentration on flax fibre weight loss after alkalinisation

Table 4-8 presents the effect of flax fibre pre-treatment (alkalinisation) on the mechanical properties of the manufactured composites. Fibre content is kept at 30 wt%. The ratio of MAPP:NF is kept constant at 1:10 using Type (A) granules of MAPP coupling. Tensile E-modulus improves with 6–9% for the three types of fibres. Only sisal shows a decrease at 10% NaOH treatment. This may be contributed to the excess removal not only of surface impurities but also of lignin [Tah07b]. Therefore sisal, which has already higher content of lignin playing a positive coupling role, was the most influenced one. Excessive NaOH in a way or another decreases the binding between the fibrils and make them move more freely and hence decreases the overall tensile E-modulus. Another tentative explanation is due to the excessive loss of weight of fibres after alkalinisation which in turn reduces the load transfer efficiency. This suggests that there are two influencing factors on the mechanical effect. First is the increasing number of sites ready for coupling and adhesion with the natural fibres with the increase of NaOH concentration%. Second is the negative effect of delignification (hence fibrillation and void formation) caused by alkalinisation. Both factors act against each other. Therefore plateau form is found for both flax and hemp while sisal reaches its saturation level of NaOH treatment at 5% concentration. 5% NaOH pre-treatment seems to be sufficient for the three types of fibres.

On the other side, strength behaviour is positively affected with increase of NaOH% till 10%. For example, sisal strength improves 8% at 10% NaOH treatment whereas sisal E-modulus decreases 8% between 5 and 10% NaOH treatment. Flax and hemp still show an obvious enhancement in strength. Hemp has a linear trend increase while flax shows a plateau form. E-modulus behaviour reaches its optimum before that of the strength. E-modulus is positively affected by the high

fibre orientation at the surfaces of the injection-moulded samples [Tah07b]. On the other side, improvement in strength depends on the increasing coupling sites between fibres and matrix with more alkalinisation.

From the results presented in Table 4-8, a concentration of 5% NaOH is selected as an optimum to be adopted because the improvement attained by the increase of NaOH concentration from 5% to 10% is not significant especially in E-modulus results for all types of fibres or strength results for flax. Therefore 10% pre-treatment is not so attractive and 5% is enough to be selected as a constant NaOH concentration pre-treatment. Also from Table 4-8, it can be inferred that sisal out of the three fibre types is the least sensitive fibre to the alkalinisation treatment in comparison to the flax and hemp fibres. The significance of the results listed in Table 4-8 was tested by two tailed t-test with 95% confidence. T-test proved the significance for the pairs (0% vs 5%), (5% vs 10%) and (0% vs 10%).

Table 4-8. Effect of NaOH concentration on the mechanical properties of PP/30% flax / 3% MAPP (Type A)

Fibre	Fibre [wt%]	NaOH [%]	E-modulus [MPa]	Dev. [MPa]	UTS [MPa]	Dev. [MPa]
Flax	30	0	5178.0	344.4	40.1	1.3
Flax	30	5	5631.4	502.8	43.1	0.9
Flax	30	10	5701.4	304.1	44.1	0.4
Hemp	30	0	5231.7	203.5	41.1	0.9
Hemp	30	5	5608.7	180.1	42.9	1.1
Hemp	30	10	5702.7	158.8	46.0	1.0
Sisal	30	0	4928.4	417.7	38.0	0.5
Sisal	30	5	5205.9	247.6	38.9	1.4
Sisal	30	10	4794.9	147.3	40.8	1.0

4.2.4 Effect of fibre type and content

Figure 4-10 presents the mechanical properties spectrum of the 30% and 50% natural fibre polypropylene composites with the use of type (A) MAPP of 1:10 ratio pre-treated with 5% NaOH.

Figure 4-10a presents the E-modulus results. Addition of fibres enhanced the E-modulus from almost 1.5 GPa to 5.2–5.6 GPa for the 30% natural fibre loading and 7.6–8.5 GPa for the 50% loading. Flax and hemp have close E-modulus results for both fibre loadings 30 and 50% with a slight superiority of 7–12% in comparison to the sisal behaviour. Fibre content has obviously a positive effect where the 50% loading has E-modulus 42, 53 and 46% more than those of the 30% loading for flax, hemp and sisal respectively.

Figure 4-10b shows the strength results. Again the coarser sisal fibres show the least strength compared to the bast fibres flax and hemp. However sisal has the largest increase in strength. The strength of the 50% sisal is 25% more than the 30% sisal, whereas the 50% flax and hemp have 18 and 19% improvement compared to the 30% flax and hemp. Close strength results for flax and hemp because both fibres' constituents and size are similar. This significant increase of strength specially with the 50% flax can be contributed to the surface matrix adhesion efficiency and its impact on the load transfer mechanism [Tah08], [El-09a].

Figure 4-10c shows the elongation of composites. The elongation of the 50% composites decreased to almost half of the values attained by 30% composites. Flax has relatively greater elongation. This can be attributed to the difference in the inclination of the fibrils to the stem axis [Cha10b] where greater angle induce more elongation and less strength.

The above results of increasing E-modulus and decreased elongation lead to a slight decrease in impact at 50% group, shown in Figure 4-10d.

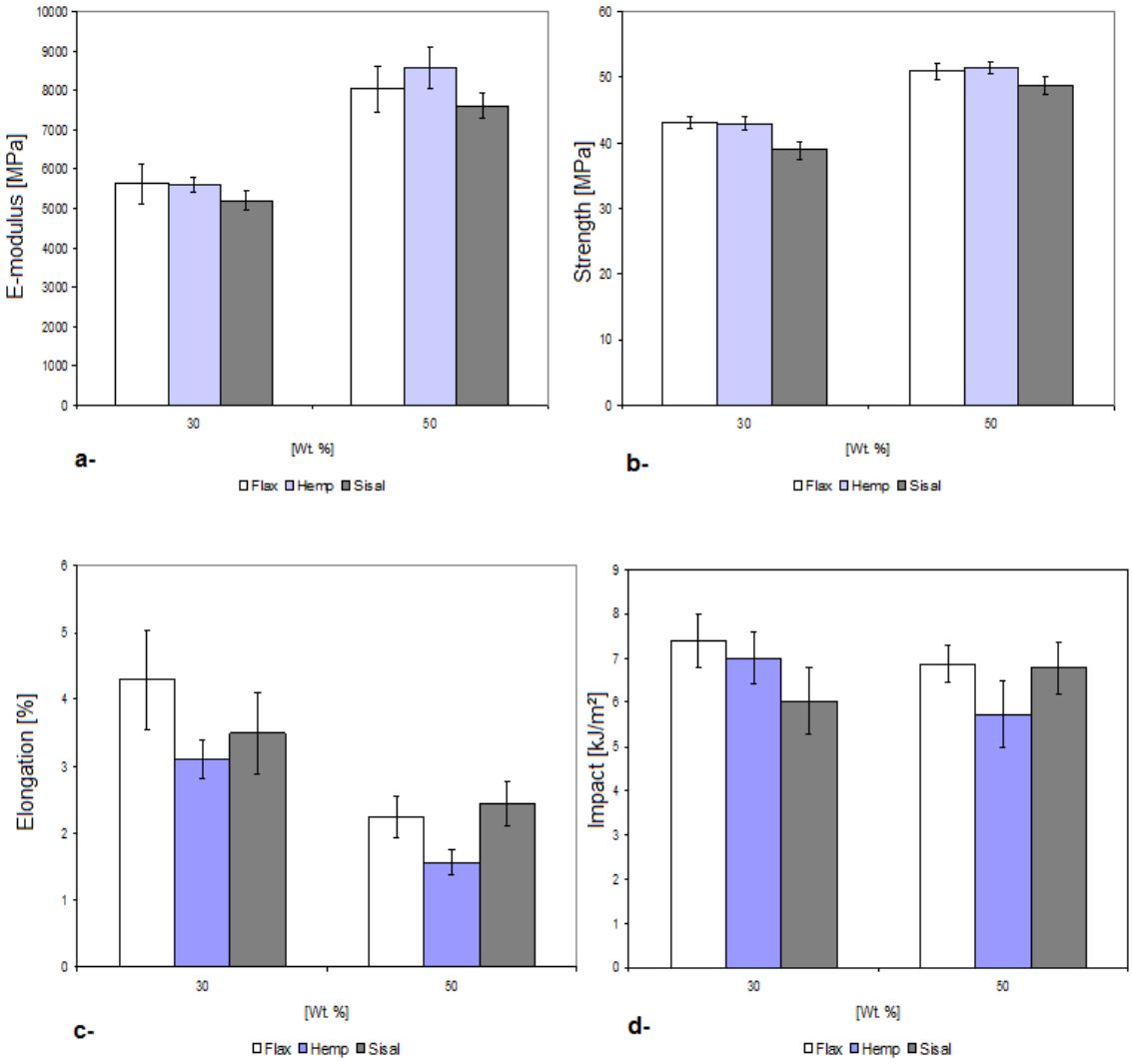


Figure 4-10: Effect of fibre type and content at 5% NaOH on a- E-modulus b- Strength c-Elongation % d- Impact.

4.2.5 Discussion of the effect of MAPP: NF ratio

This part deals with the main problem claimed in this section which is the diversity in the optimisation rules for implementing the MAPP as a coupling agent in the natural fibre thermoplastic composites. Maximum value of the curve plateau is considered the optimum value. Table A- 1 in Appendix lists all the results of the mechanical properties for the prepared composites at different MAPP:NF ratios considering also the effect of fibre type and MAPP type.

It is noticed here that the improvement in the mechanical properties like E-modulus or strength is much lower than that reported in section 4.1 (Treatment of extruded natural fibre / polypropylene). This infers the effect of both the kneading process and the kneading time on improving the fibre distribution and the success of PP to cover bigger areas of the fibres.

At each certain group of parameters (fibre content, fibre type), the optimum MAPP:NF ratio corresponding to the highest (E-modulus or strength or impact strength) is defined. The results of optimising the MAPP:NF ratio are summarised in Table 4-9. The improvement percent at the optimum value with respect to the reference value of compounding without MAPP (MAPP:NF = 0) is written next to the optimum MAPP:NF ratio.

Table 4-9. Optimum MAPP:NF ratios (Improvement %) for 30% and 50% NF.

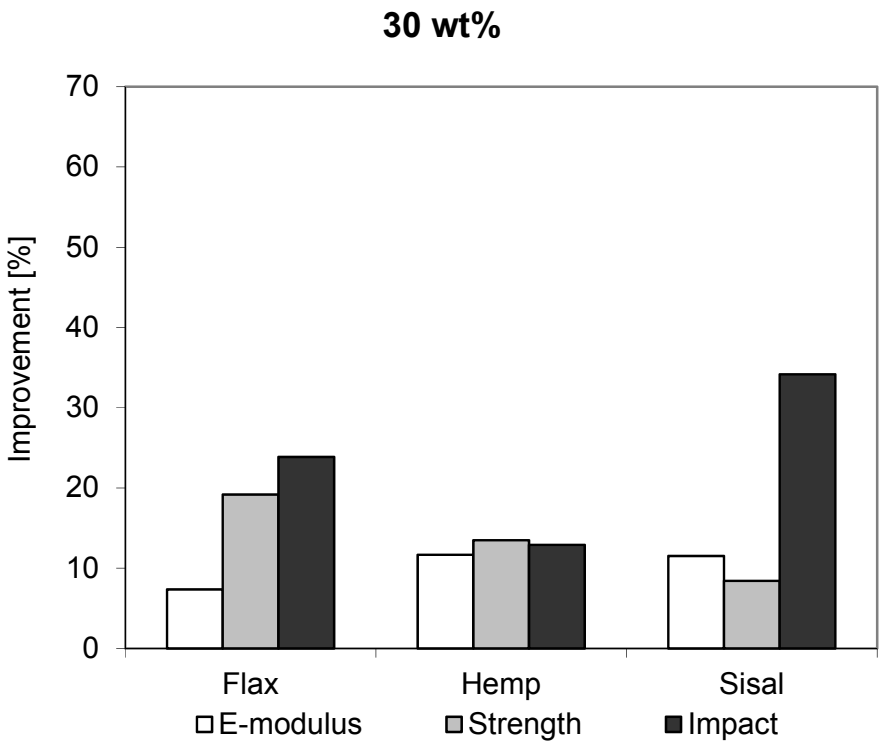
	30 wt%			50 wt%		
	Flax	Hemp	Sisal	Flax	Hemp	Sisal
E-modulus	10 (7.3)	6.7 (11.7)	6.7 (11.5)	13,3 (20.6)	10 (17.0)	16.7 (6.3)
Strength	6.7 (19.1)	6.7 (13.5)	6.7 (8.4)	6.7 (66.1)	13.3 (28.5)	6.7 (12.8)
Impact	6.7 (23.8)	10 (12.9)	6.7 (34.1)	6.7 (60.1)	6.7 (39.5)	6.7 (19.2)

From Table 4-9, it is clear that the MAPP:NF of 6.7 appears so often. Some high values appear in the 50% group like 13.3 and 16.7% values in case of maximising the flax and sisal E-modulus. However, the difference in hemp strength between 6.7% and 13.3% is less than 3 MPa. But how much is needed to increase the MAPP: NF ratio? Figure 4-11 shows the improvement percentage at the optimum MAPP:NF. In general, the optimum MAPP:NF ratio lies in the range of 6.7-10 for the both 30% and 50% fibre loadings.

It is noticed in Figure 4-11a, where the improvement of the three fibres at 30% lies in a close range relatively when compared to the deviation between flax and sisal at 50%, Figure 4-11b. This is evidence that natural fibre type and shape play an important role in the composite behaviour and cannot be considered as fillers.

Another interesting notice, E-modulus shows improvement at higher MAPP:NF where the tensile and impact strengths are getting maximised at lower MAPP:NF ratios. This remark can be explained as follows. Both E-modulus and strength increase with the increase of coupling sites (by increasing MAPP:NF ratio). However, there is a threshold stress which is limited by the fibre stress or the fibre fibrillation and hence the mode of failure changes as shown later in the SEM Figure 4-12..

a-



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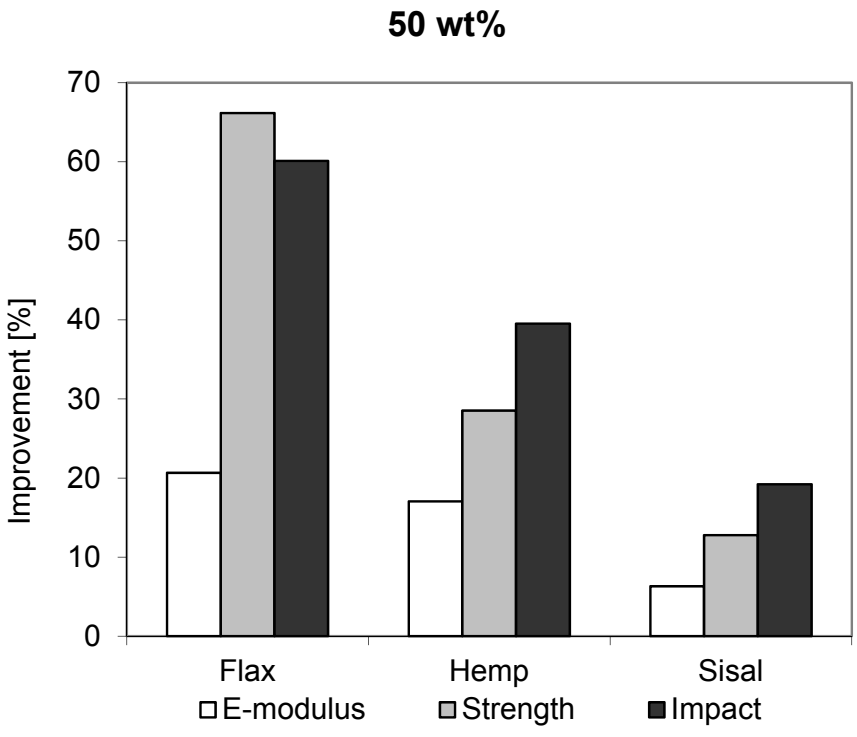


Figure 4-11: Maximum improvement in mechanical properties at optimum MAPP:NF ratios for a- 30 wt% b- 50 wt%

Figure 4-12 shows SEM fracture surfaces at different MAPP:NF ratios. Composite free from MAPP copolymer shows long pulled out fibres. At 6.7% MAPP:NF for the 30% flax, the fracture shows less pulled out fibre length and some fibre debonding sites of transversal fibres. At more MAPP:NF ratio of 16.7%, the fibres are well covered to the PP matrix and the polymer remnants are present on the broken pulled fibre surface. Also some fibres show longitudinal shear failure where fibres are fibrillated.

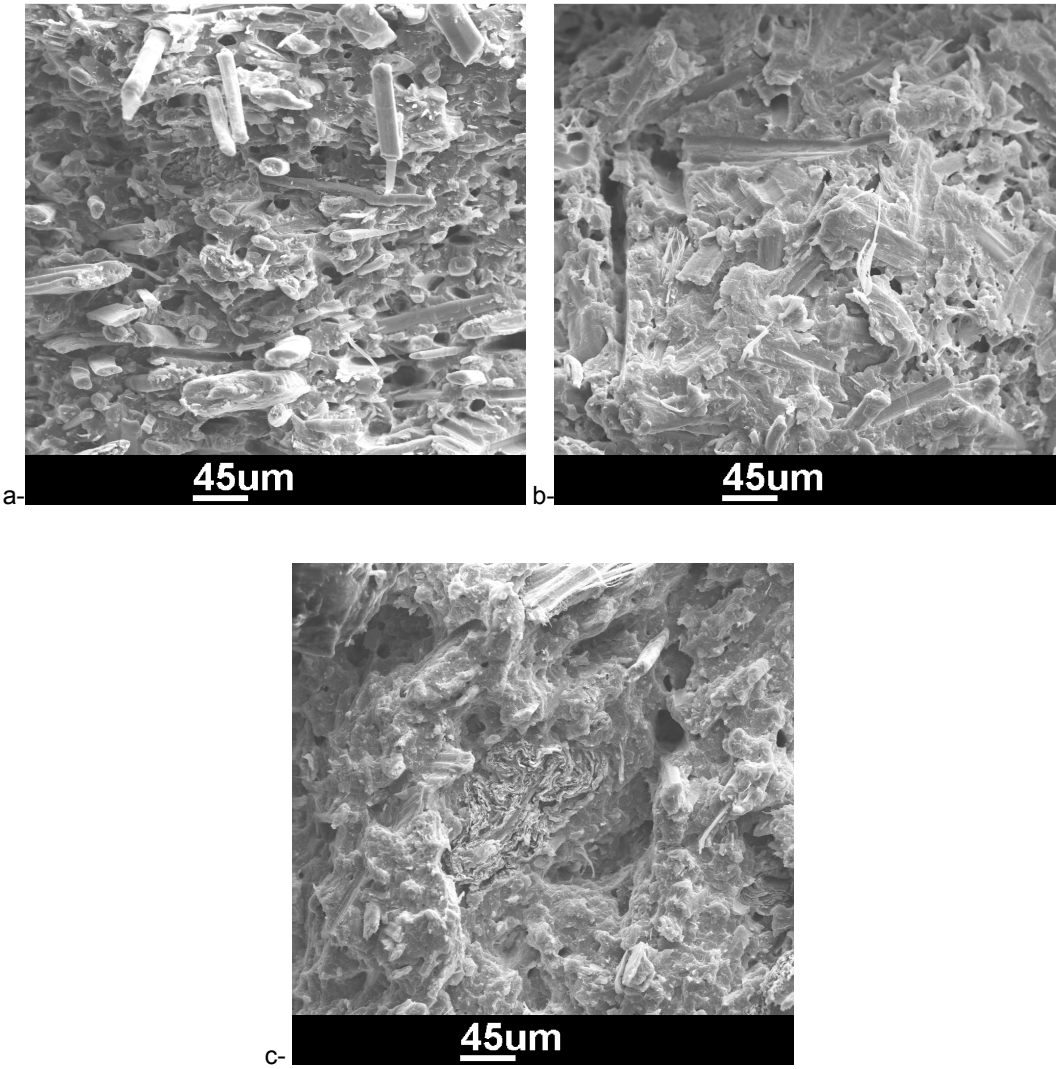


Figure 4-12: Effect of MAPP:NF ratio on impact surface a—0.0%; b—6.7%; c—16.7%

Figure 4-13 shows the TGA and the differential thermal gravimetric DTG of the flax PP composites copolymerised with granule MAPP of Type A. Decomposition proceeds by losing the absorbed water then hemicelluloses followed by alpha cellulose and finally by lignin [San09].

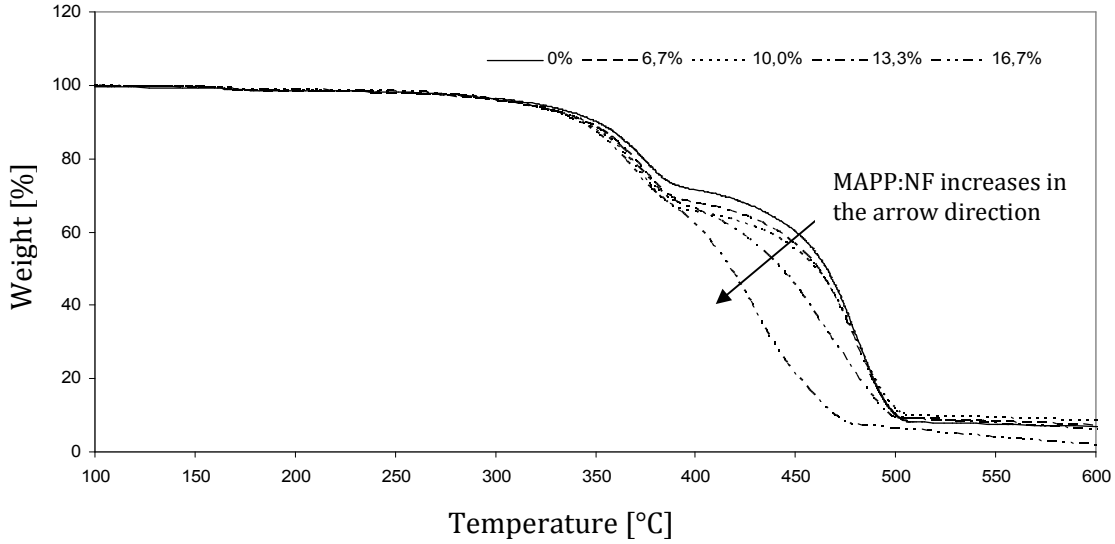
Composites show two peaks' with maxima ranging in 369.4–374.8°C and 432.4–481°C corresponding to the decomposition of flax and PP respectively. The recorded decomposition behaviour is similar to that of Doan [Doa07]. The temperatures at the peaks' maxima are decreasing slightly as the MAPP:NF ratio increases. This note is

valid for 0, 6.7 and 10% of MAPP:NF ratios. For higher ratios of MAPP:NF with 13.3 and 16.7%; the decomposition takes place at significant lower temperatures. This is an evidence that the excess MAPP induces a dispersion effect rather than a coupling effect on the fibre matrix interface as reported by [Lee09]. This also may explain why the wetting seems better although the mechanical properties are decreasing when the MAPP:NF ratio is more than optimum.

DSC results are given in Table 4-10. Results show similar behaviour reported by [Lee09]. The melting temperature decrease with the increase of MAPP:NF ratio. The reduction in temperature is too small to be felt as it is almost 0.5%. While in Figure 4-14, the melt enthalpy shows an increasing trend or even a plateau effect and a maximum value at 10% MAPP:NF then with a steeper trend goes down. The reduction in enthalpy is greater as it drops to 25% for the MAPP of Type A and 14% for MAPP of type B. This assures the TGA result of the dispersion phenomenon above 10% MAPP:NF. Interesting is also the similarity in behaviour of recrystallization where 10% MAPP:NF has the maximum recrystallization energy. This can be correlated to the maximum efficiency of coupling between the fibre and the polymer. Higher MAPP:NF decreases the recrystallization because the excess MAPP does not react with itself when the MAPP molecules do not undergo grafting [Kee04].

Table 4-10. Effect of MAPP:NF % and type on melt temperature and enthalpy of 50% flax PP

MAPP type	MAPP:NF [%]	Melt temperature [°C]	Melt enthalpy [j/g]	Recrystallisation temp. [°C]	Recrystallisation enthalpy [j/g]
Type A	0	167.31	51.46	132.26	67.36
	6.7	167.00	54.55	128.87	70.94
	10	166.86	58.66	129.18	75.65
	13.3	166.28	56.00	128.99	69.36
	16.7	166.62	44.97	128.19	61.01
Type B	0	167.81	51.46		
	6.7	166.42	48.75		
	10	164.51	58.87		
	13.3	165.69	50.48		
	16.7	164.29	50.84		



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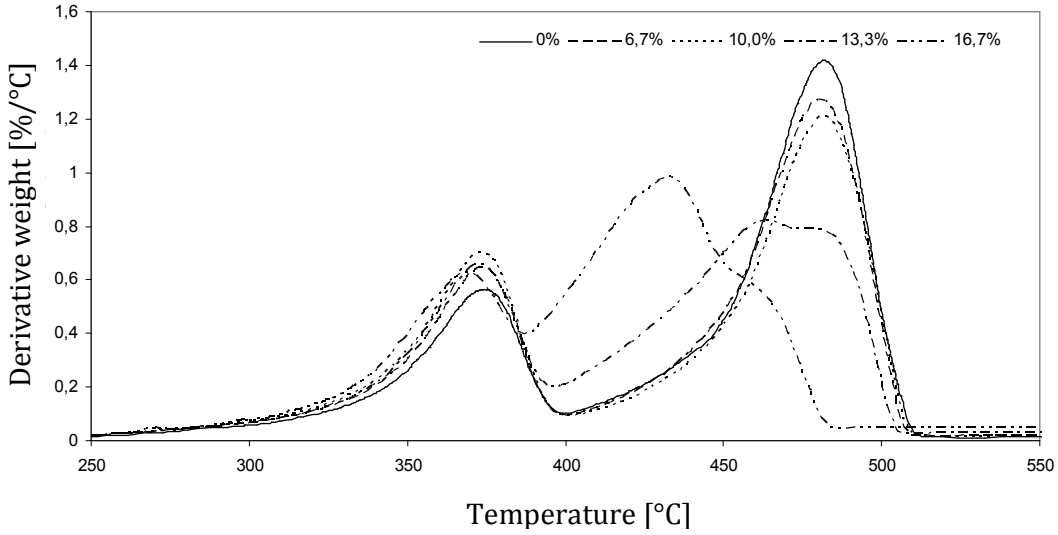


b-

Figure 4-13: Effect of MAPP:NF ratio for 50% Flax PP composites coupled with MAPP (Type A) on a—TGA; b—DTG.

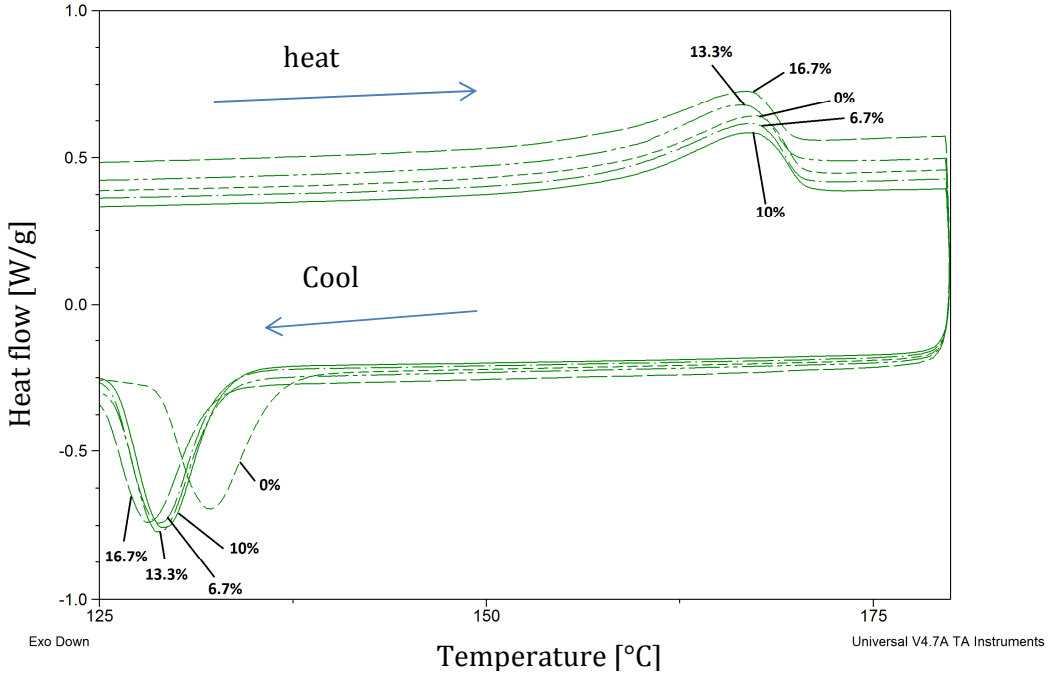


Figure 4-14: DSC results of MAPP:NF ratio for 30% Flax PP composites coupled with MAPP (Type A).

4.2.6 Effect of Copolymer Type

For the sake of comparison between MAPP types A and B, Figure 4-15 and Figure 4-16 shows the mechanical properties corresponding to both 30% and 50% flax with the different forms of the MAPP. Granulate MAPP, Type A, always shows near parabolic forms with optimum values while the powder MAPP, Type B, shows that even after reaching the optimum value, constant or slightly increasing trend is still going on. Figure 4-16a and Figure 4-16b show the E-modulus behaviour for both fibre loadings of 30 and 50%. Type B does not impart improvement for the 30% composite E-modulus whereas Type A imparts almost 7% improvement at the 6.7% MAPP:NF ratio. For the 50% fibre loading, both types A and B result in an improvement namely 20% and 15%. It is important to note that the optimum MAPP:NF ratio is the same for the 30 and 50% fibre loadings.

Figure 4-16c and Figure 4-16d show the strength behaviour. Type B has a better effect than Type A on the composite strength. Type A has a faster strengthening effect than Type B. Type A has its optimum MAPP:NF ratio of 6.7% in the 30% composite whereas Type B has a slower response and reached its maximum at 13.3%. In case of 50% composite, Type A again has a maximum point at 6.7% of MAPP:NF. The Type B shows an increasing linear trend of composite strength in the range of 6.7–16.7% without reaching an optimality point. Figure 4-16a shows an interesting observation. Type A composite has a decreasing elongation with more MAPP:NF whereas the Type

B has a softer effect where the elongation slightly changes in the 30 and 50% fibre loading composites. The same behaviour for Type A and B is observed in Figure 4-16b with lower elongation values. Figure 4-16c shows the impact results of the un-notched specimens for the composites filled with 30% flax. Both types A and B are coincident in the 0-6.7% range then Type B continues positively in comparison to Type A. Again the same behaviour is repeated in Figure 4-16d for the 50% filled composites. However, the change is less positive for Type B and negatively for Type A.

The better behaviour of Type B in general can be attributed to the better thermal stability of the composites with higher molecular weight of the powder form MAPP. As mentioned earlier; Type B has normally lower acid number and hence higher melt flow index MFI, better mixing, and better diffusion [Gue04]. This explains the good impregnation of the coupling inside the fibres. Type A shows a drop in strength after reaching the maximum value because excess MAPP does not result in more coupling with fibres but results in self-reaction leading to weak layers instead. Type A has faster thermal degradation as shown in Figure 4-13. This is due to more MAPP: NF compared to the more thermal stability of MAPP Type B, as shown in Figure 4-17. The DTG curve, shown in Figure 4-17b, shows two peaks with ranges of 357.3–374.8°C and 480–486°C. The increase of MAPP:NF ratio to 16.7% leads to 48°C reduction of the thermal stability which is less than 6°C reduction for the Type A composites. The result, that Type B has higher thermal stability, matches the results of Kim [Kim07] where the lower molecular weight copolymer has lower thermal stability behaviour. Excessive MAPP:NF does not impart enhancement of composite strength and impact. It is also noted that the change in the first peak around the 370°C is more affected in case of Type B. This is also matching with the results of Lee [Lee09] who worked with bamboo fibre PP composites.

DSC results are given in Table 4-10. Results show similar behaviour reported by [Lee09]. The decrease in melting temperature and enthalpy is slightly larger in MAPP of Type B compared to Type A. This is attributed to the more reaction and higher diffusivity of Type B [Cha10b].

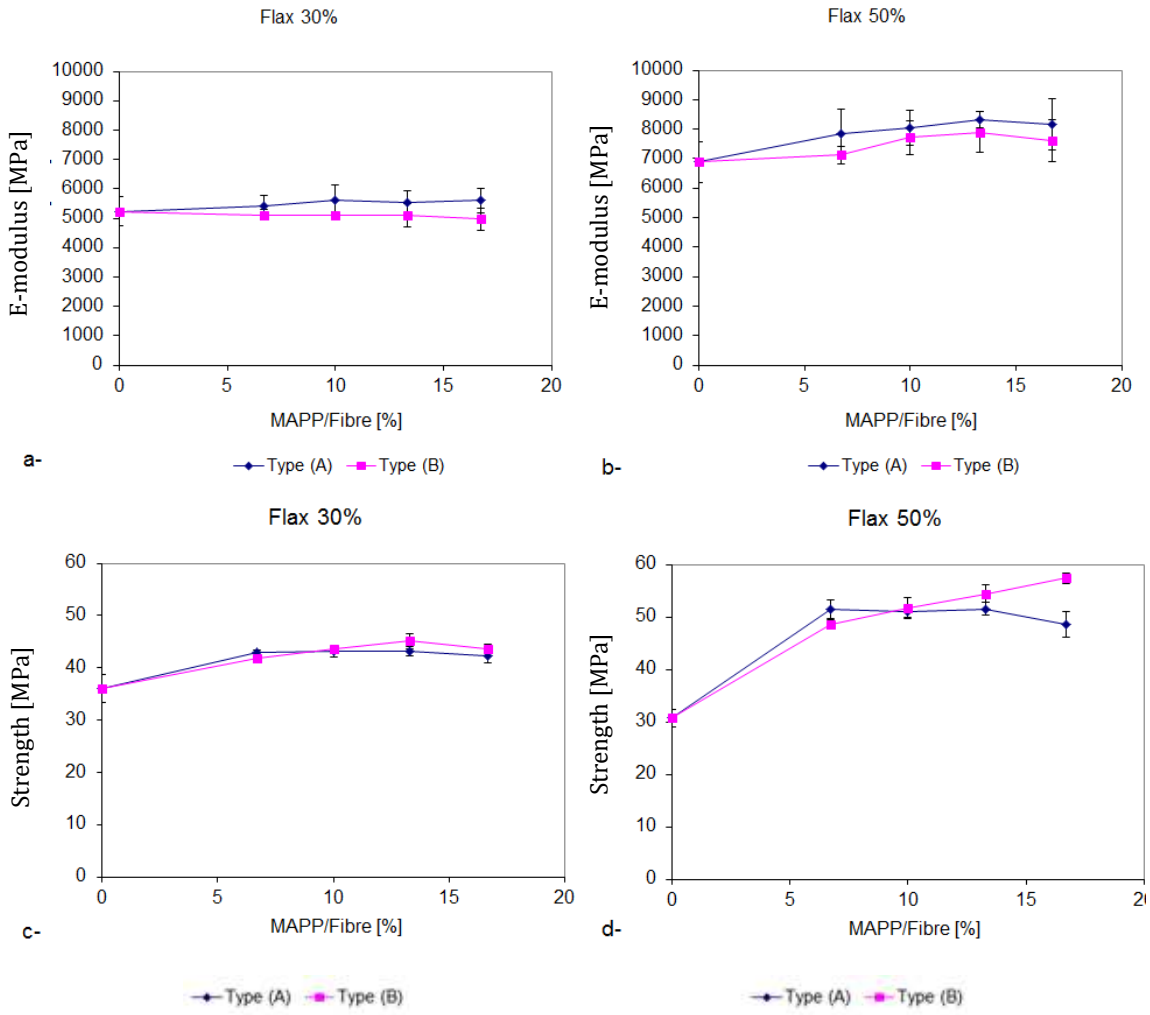


Figure 4-15: Effect of MAPP:NF on a,b- E-modulus c,d- Strength for both types of MAPP at 30 and 50% flax.

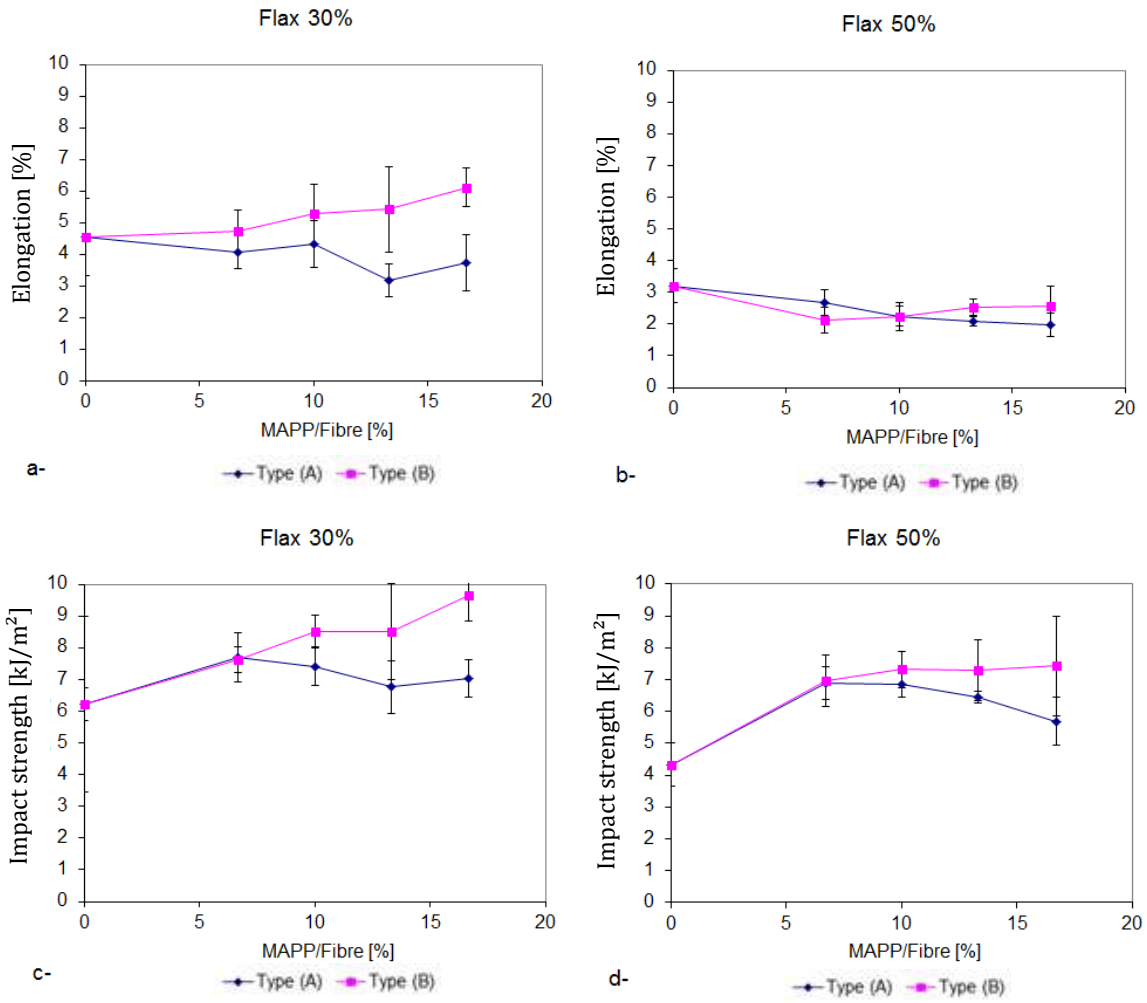
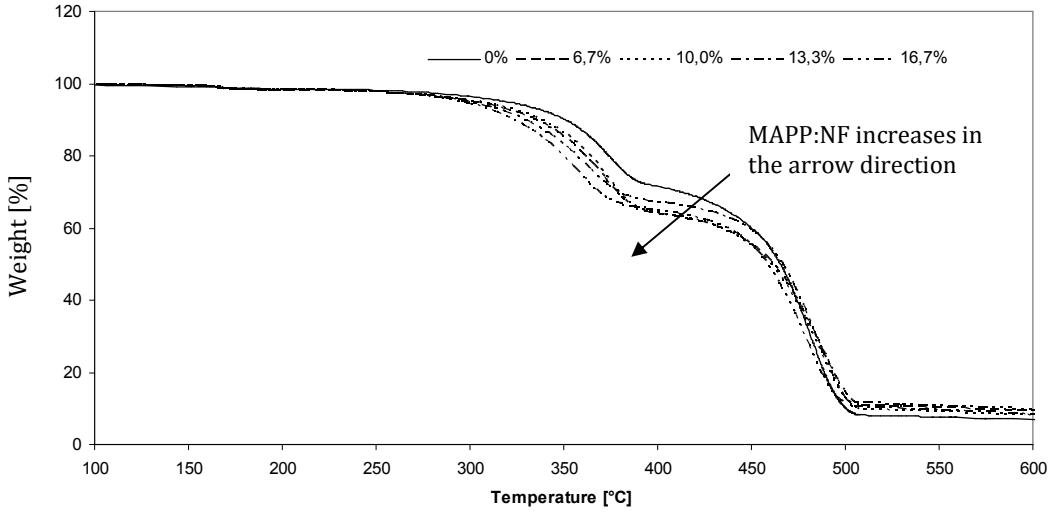
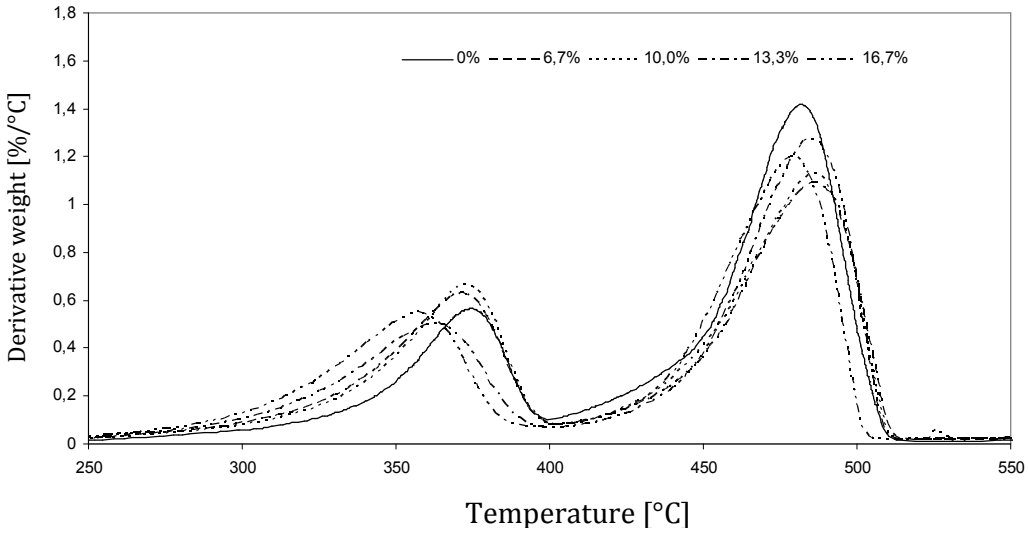


Figure 4-16: Effect of MAPP:NF on a,b- Elongation c,d- Impact for both types of MAPP at 30 and 50% flax.



a-



b-

Figure 4-17: Effect of MAPP:NF ratio for 50% Flax PP composites coupled with MAPP (Type B) on a- TGA b- DTG.

Finally, the effect of copolymer type on the water absorption level by natural fibre thermoplastic composite. Figure 4-18 shows better behaviour for the granule Type A MAPP where the water absorption of Type B composites is about 16% more than those of Type A composites. A decreasing trend is noticed with the increase of MAPP:NF ratio. This points out to sufficient interface reaction due the Type A copolymer compared to the Type B. This is attributed to the high MA grafting of Type A [Kim07].

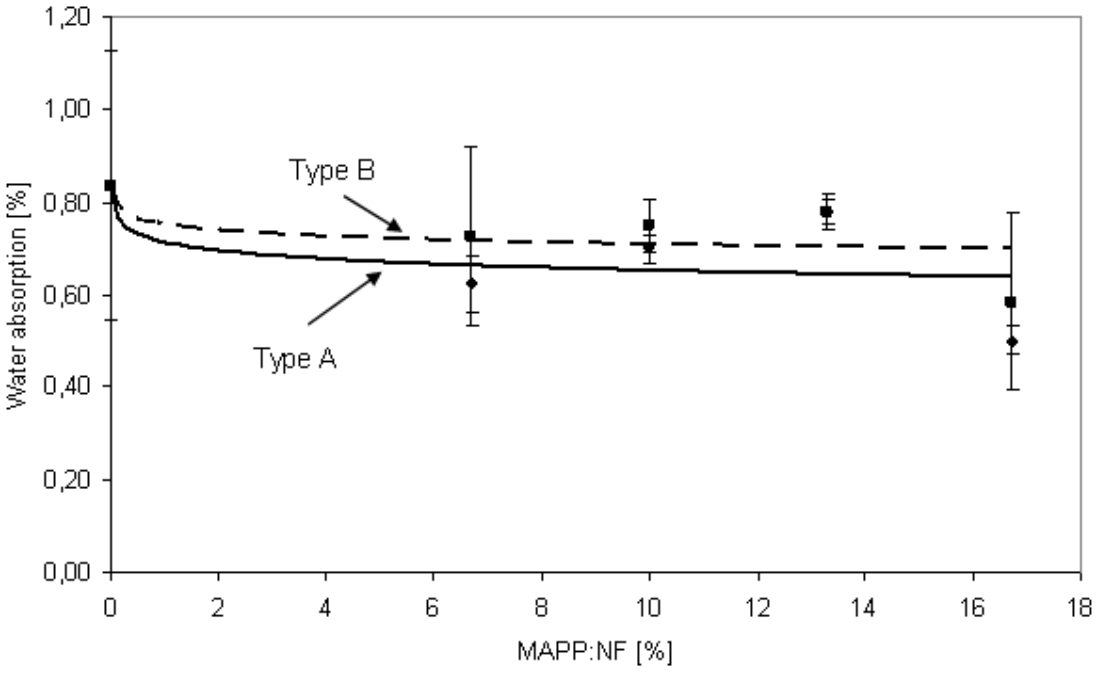


Figure 4-18: Effect of MAPP:NF ratio and MAPP type on water absorption.

Figure 4-19 shows the scaled estimates using JMP. Fibre and MAPP types are considered categorical factors. Fibre content, NaOH and MAPP:NF are considered discrete variable. The interaction effect between factors is studied. The significance of MAPP:NF, NaOH and fibre content is denoted by the arrows in the left side. Afterwards, the significance of MAPP type and the fibre type effect appears when combined with other factors like NaOH and MAPP:NF.

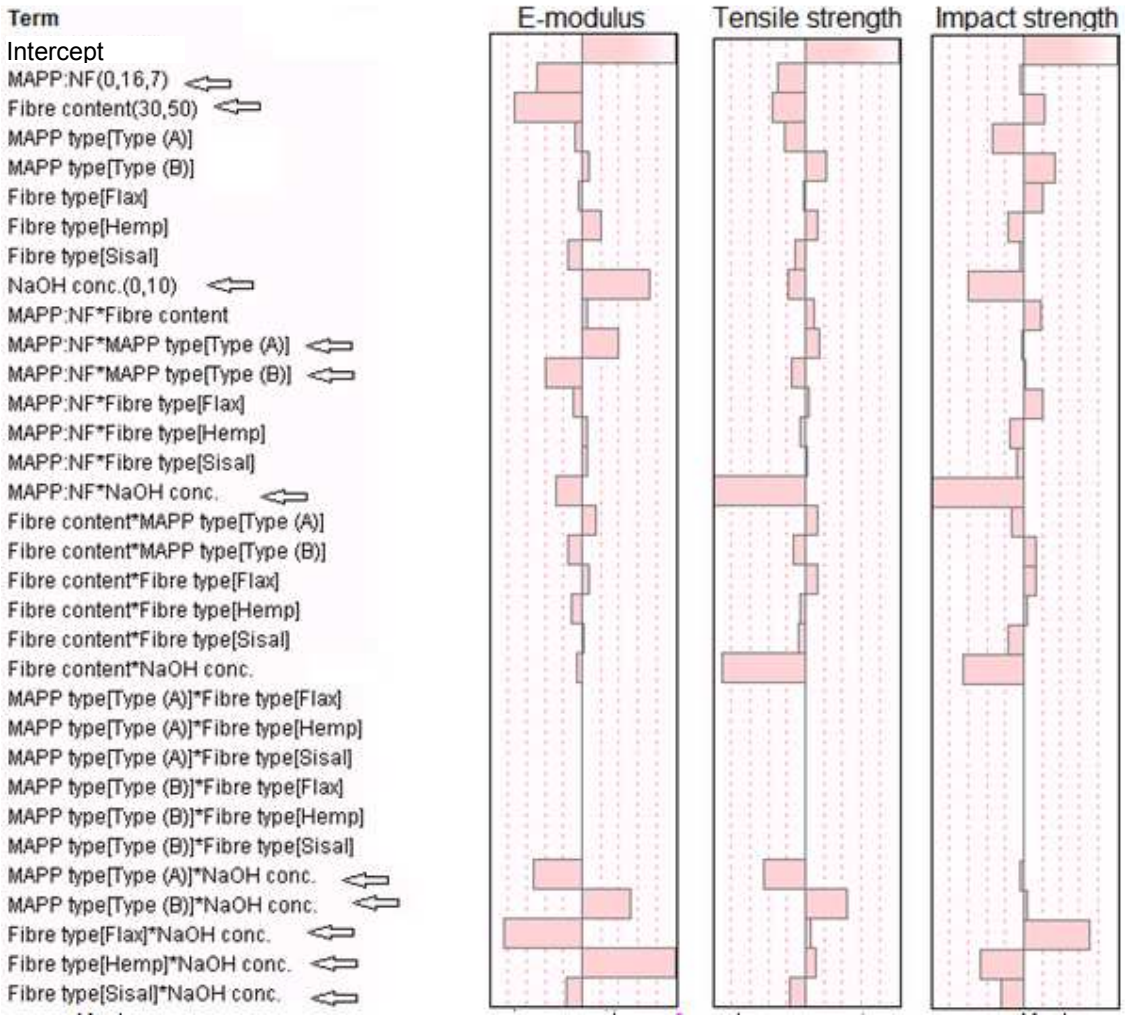


Figure 4-19: JMP analysis of scaled estimates

4.2.7 Outcomes

The behaviour of the NFTC mechanical properties is dependent on the fibre type. In other words; fibre type plays an important role in the strengthening and cannot be considered as fillers only. Pre-treatment of 5% NaOH for 24 days at room temperature is sufficient to have more efficient fibre surface for coupling with the thermoplastic

matrix and hence further processing. The optimum MAPP:NF is searched for and the following points are deduced:

1. MAPP: NF ratio of 6.7% is enough for having a significant improvement in mechanical properties and water absorption. However for reaching Maximum value in the studied property (E-modulus, strength, impact), more MAPP:NF ratio is needed as listed in Table 4-9. 10% ratio of MAPP:NF should be appropriate for future work.
2. In general, it is noticed that the required MAPP:NF ratio for maximising the E-modulus is less than that needed for maximising both tensile strength and impact strength properties. This is explained in terms of the changing failure scenarios from pull-out to fibre break-up till the fibrillation of the fibre as shown in SEM photographs.
3. Granule Type (A) MAPP is better in the range of [0–6.7%] for E-modulus and strength and vice versa. For impact, both types go on coincidently then type B composites result in higher impact properties. Composites of high percentage Type B MAPP have higher thermal stability than the Type A composites. This is related to the more molecular weight of Type B. Water absorption of the Type A MAPP natural fibre composites are better than the Type B MAPP composites

Briefly; the important outcome of this section is the definition of 10% MAPP:NF ratio. This means for 30% composite; MAPP is (30 x 10/100=3%) and for 50% composites; MAPP is (50 x 10/100=5%).

5 Definition of the Compounding Process Parameters

Compounding of PP with natural fibres is carried out by different methods as mentioned in 2.3.2. The main compounding methods are kneading, Henschel kinetic mixer, pulltrusion and extruder. Kneading is the main technique used for compounding on the laboratory scale. On the other side, the extrusion is the favourite compounding method on the industrial scale. A review will be made for both methods. But more focus and parametric study will be done for the extrusion.

5.1 Influence of kneading on NFTC (Literature review)

The main processing parameters to be optimised in kneading are the mixing speed, time, temperature. The effect of the kneader mixer type (cam, Banbury, roller) will not be studied because it is a common practice which already theoretically proved that the fibre distribution is maximised by using the roller type kneader [Ahm11]. Although a lot of literature is reporting the compounding and the characterisation of the PP/ Natural fibre composites by kneading, but it is rare to find a parametric study. Table 5-1 lists some of these references like [Gar02] [Arb05] [Bar10] [Yan13] [El-13d]. As seen, there are different and divergent conditions of kneading parameters despite the use of the same system of PP and bast fibres like flax and hemp.

Yan [Yan13] tried to optimise these parameters as shown in his study. It is concluded that keeping the temperature at a level just above the matrix melting point besides to the least mixing time but with higher shear rate will guarantee higher mechanical properties. It can be controversially said that higher mixing temperature and longer mixing time can ensure better fibre distribution due to the lower polymer viscosity. However fibre thermal degradation is expectedly aroused by high temperature and long kneading time. The issue of using high shear rate needs to be also optimised because increasing the shearing will impart a positive effect which is the increased friction and interaction energy of fibre and fibre/matrix. However excessive shearing can damage the fibre aspect ratio and decrease the molecular chain of the matrix polymer. It can be inferred from this study [Yan13], that the optimisation directed the processing parameters to be relatively close to those of the Henschel kinetic mixer where the fibres are mixed with the polymer in a low temperature with high shearing to get benefit of the evolving kinetic energy.

El-Shekeil [El-13d] studied similarly the optimisation of polyester/ kenaf composite. Almost similar results are obtained where the lower temperature and the higher shear rate are found to be optimum. Mixing time is found to be the middle level but additionally he studied the effect of the fibre size as shown in Table 5-1. Additionally, statistics showed that processing temperature was the most significant parameter affecting the production of polyster kenaf composite. The fiber size was the second parameter. Processing speed and time were least significant in producing the composite. Other optimisation studies are also reported but considering other polymer natural fibre composites.

Table 5-1. Literature about thermolplast/natural fibre composites by kneading

Reference	Material	Notes
2002, Garkhail[Gar02]	PP: XY6500T Shell, MFR=35 Flax Duralin MAPP Polybond® 3002	the polymer (blend) / flax fibre combination were blended for 30 min at 210°C in a kneader (HBI System 90) at 30 rpm.
2005, Arbelaiz et al.[Arb05]	PP HV200, Solvay, MFR=10 Flax From Finflax MAPP Epolene E-43 in 1:20 ratio with flax	Haake Rheomix 600 with two Banbury rotors at 180 8C and after loading all components, they were mixed for 5 min at 40 rpm
2010, Barkoula et al.[Bar10]	PP from Stamylan (MFR=47) Flax 10 mm MAPP 3% (Polybond 3150)	PP is blended with flaxin a Haake Kneader (model-HBI System-90) at 30rpm for 30min at 210°C
2013, Yan [Yan13]	PP M800E, Sinopec, China) Hemp < 28 mm China-Hemp Industrial Investments MAPP: 5% Bondyram1001	pre-heated internal mixer (XH-409, Dongguan City Xihua Testing Machine Co. Ltd, China). Temperature (165-170-175°C) Mixing time (12-16-20 min) Speed (30-40-50 rpm) Optimisation using Anova is at 165°C/12 min/50 rpm
2013, El-Shekeil [El-13d]	Polyester based thermoplastic polyurethane Kenaf bast fiber was obtained from KEFI (M) Sdn Bhd, Setiu, Terengganu, Malaysia	Haake Polydrive R600 internal mixer Temperature (180-190-200°C) Mixing time (11-13-15 min) Speed (30-40-50 rpm) Fibre size (<125-125 to 300- 300 to 425 µm) Optimisation using Taguchi is at 180°C, 50 rpm, 13 min, 125-300 µm size

5.2 Influence of extrusion on NFTC (Literature review)

Kneading as a compounding technique is suitable for the laboratory level due to the better control on the added constituents and the processing parameters. However from the industry point of view, extruder represents the first selection for its mass production capability. Therefore this section will focus on optimising this process with respect to PP/ flax composite.

It is always believed that the effect of the compounding parameters on the resulting mechanical properties can be interpreted by the help of change in fibre length or fibre aspect ratio [Bos04]. The fact is not so direct and easy [Bar10] because there are other factors (such as cellulose degradation [Sah99], gas evolving, fibre orientation, adhesion quality and new coupling sites) which play also a role on the load transfer between matrix and fibre. Besides, the change in the composite properties due to the change in the compounding parameters cannot keep its significance when the composite is granulated and further processed in injection moulding. However in case of extrusion end-products like roofing profiles, it is strongly assumed that the fibre size (length, diameter, length to diameter ratio that is called aspect ratio) will have a great effect on the resulting mechanical properties.

This strong belief is based on two concepts:

- The common rule of mixture which explains the increase in composite strength by the share of the added fibres, fibre adhesion and fibre orientation.

- The critical shear length of the fibre where the fibre can transfer loading only when its aspect ratio exceeds a certain limit as explained in section 2.5 and Figure 2-18.

This simple rule of mixture is exposed to many modifications [Sah99], [Kel65] regarding the fibre length, orientation and coverage efficiency with the coupling agent. Fibre and orientation efficiency factors are introduced in Kelly-Tysson formula, Equation 5-1 and Equation 5-2 for both E-modulus and strength. They are found to give more matching with the experimental results [Kel65]. Other modifications are suggested and implemented by El-Sabbagh [El-09a] and [Gra14]. More details are given in section 2.5 and Equation 2- 3 till Equation 2- 9.

$$E_c = E_m(1-v_f) + \eta_{oE}\eta_{lE}E_f v_f$$

Equation 5-1

$$\sigma_c = \sigma_m(1-v_f) + \eta_{o\sigma}\eta_{l\sigma}\sigma_f v_f$$

Equation 5-2

More details about the previous equations and how to find out the corresponding efficiency factors in cases of E-modulus and strength calculations are given in section 2.5 and Equation 2- 3 till Equation 2- 9.

Most of the researchers used the mean values of the fibre lengths [Kel65], [Gla99], [Bos04]. Only Andersons [And06] who has used Weibull distribution in order to describe the fibre length population and hence to define the fibre portions below and above the critical fibre length. Andersons investigated extruded flax roving-polypropylene composites at 180-200°C at ZSK 25 WLE twin screw extruder. Some conditions of the extruder are missing namely; speed and extruder elements. The effect of different extruder designs and shear rates was not studied by Andersons [And06].

Beaugrand [Bea13], [Ber14] carried out experiments on low melting polymer PCL with chopped Hemp fibres using severe and light kneading configurations at different speeds, temperature and feeding rates. The fibre failure method by either fragmentation in the cell wall or the decohesion in the inter-fibre cement was correlated with the fibre aspect ratio. Beaugrand [Bea13] expected firstly that there will be a linear trend relation between fibre aspect ratio and the mechanical property. Thus the severe kneading screw configuration should result, according to his expectation, in low aspect ratio and hence lower breaking stress. Surprisingly, the breaking stress is higher than that of the light kneading configuration. Beaugrand [Bea13] justified his finding that L/D ratio does not give full description of stress transfer. He expected that lower aspect ratio with more fibrillation (as a result of severe kneading) creates more load bearing interfaces and hence higher breaking stress is attained. However, it should be recalled that PCL processing temperature is less than the temperature profile in PP natural fibre composites, presented in this study. High temperature applied in case of PP, will result

in thermal decomposition of the cement wall bonding between fibres. Hence fibrillation takes place and high aspect ratio can be expected. This improvement in aspect ratio will be attributed to the effect of the applied temperature and not just shearing effect. This factor should be considered in the suggested simulating tools [Bea13].

In the next section, an experimental study is carried out to study the effect of the extrusion processing parameters on the final composite mechanical properties as and the development in the fibre dimensions.

5.3 Material preparation

Flax fibres in sliver form, MAPP (Type B), optimised in section 4.2, as a coupling agent and PP MFR 52 are the materials used in this section. Their data are listed in section 3.2. Flax slivers are cut to 10 m length, then alkalinized with a solution of 2% sodium hydroxide overnight. The fibres are then washed with distilled water and neutralized. Drying takes place in two steps; first left in ambient air for 24 hours and then left at 80°C for another 24 hours.

MAPP is mixed with PP bearing in mind that MAPP : Flax is 1:10 wt/wt. Figure 5-1 illustrates the sequence of compounding where the PP/MAPP previously mixed are fed through input hopper and then the fibres are inserted from the extruder side opening. The temperature pattern is 180-190-190-200-210-220-230-230 °C from input to output zones.

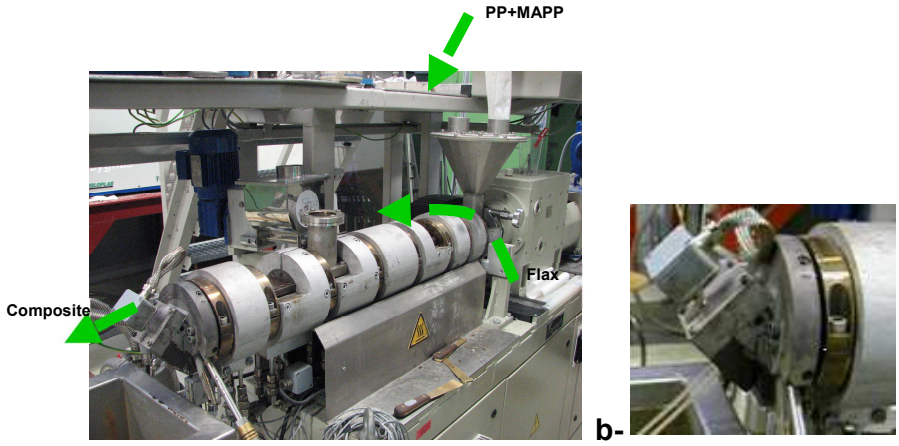


Figure 5-1: Compounding procedure of PP and Natural fibre at Berstorff ZE25Ax40D a- Overall photo b- Extruded two strands

To control the fibre content (FC) of the extruded NFTC, an empirical formula, Equation 5-3, is developed. The fibre content is a function of the flax sliver linear density, screw speed (n), thermoplastic granules feed rate ($\dot{FC}_{pp}$) and finally a constant (a) which is related to the geometry of the extruder.

$$FC_{NF} = \frac{FC_{NF}}{FC_{NF} + FC_{pp}} = \frac{\dot{FC}_{NF}}{\dot{FC}_{NF} + \dot{FC}_{pp}} = \frac{1}{1 + \frac{\dot{FC}_{pp}}{\dot{FC}_{NF}}} = \frac{1}{1 + \frac{\dot{FC}_{pp}}{a \frac{\partial FC_{NF}}{\partial x} n}}$$

Equation 5-3

To validate this function before executing the planned experiments, preliminary compounding extrusion is carried at different fibre contents namely 10, 20 and 30 wt%. The actual fibre contents are then compared against the theoretical values to check the validity of equation (4). Figure 5-2 shows that the error in the trend lines of fibre content estimation is tolerable (almost 5%), regardless the different fibre contents and different screw layouts.

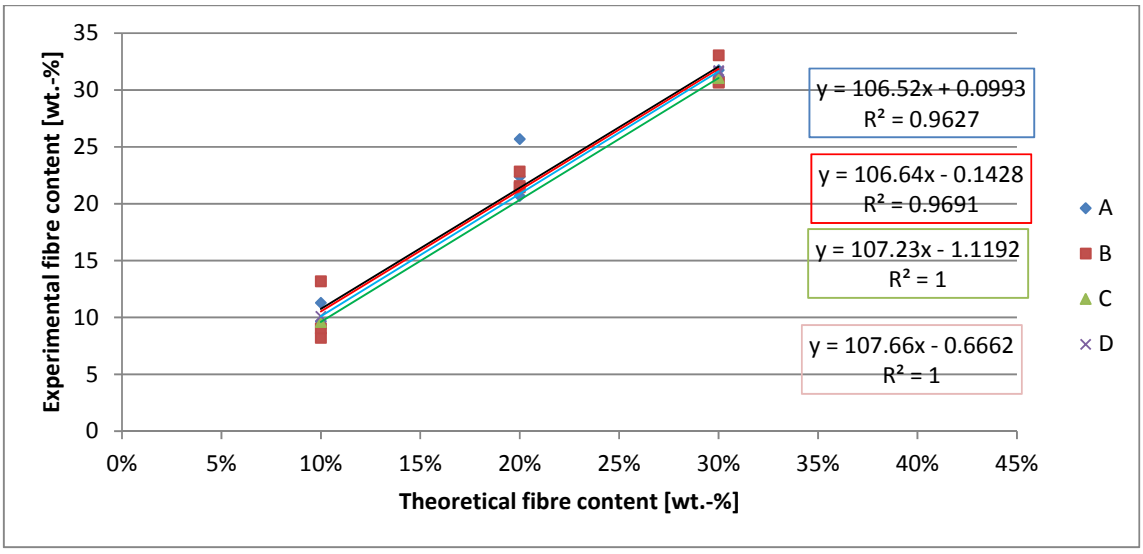


Figure 5-2: Comparison between the real and the theoretical fibre contents

Table 5-2 illustrates the plan of the investigated parameters namely; speed, fibre content and extruder layout. Screw layout effect is investigated in four arrangements. The common feature between the extruder designs is the use of the conveying elements with descending width pitches (37.5 mm to 25 mm pitch) in order to ensure material transport at the beginning then pressure build-up in the metering section at the output die. Second common feature is the presence of reverse element to produce a significant back pressure and to guarantee that the elements in front of the reverse element are fully filled with the melt. This allows also the use of the vacuum pump to remove the evolving gases from the product.

Table 5-2. Studied parameters affecting the extruded fibre size and final properties

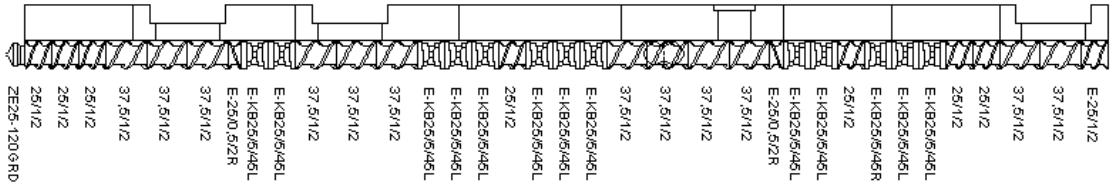
Parameter	Alternatives
Screw layout	A/B/C/D
Screw speed [rpm]	100/200/300
Fibre content [wt%]*	10/20/30

* The fibre content is calculated in terms of the fibre linear density (weight in g/m), screw speed (rpm) and PP feed rate (kg/hr) as shown in Equation 5-3.

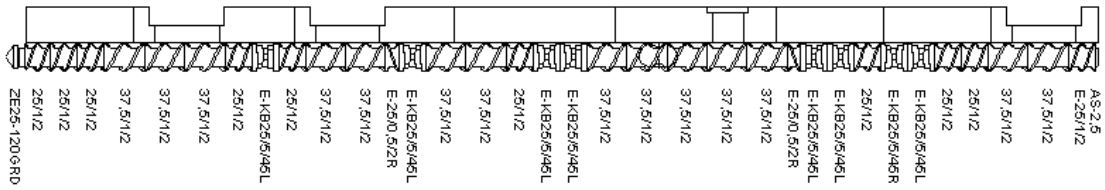
Layouts (A) and (B) have different numbers of kneading elements which are responsible of mixing. Only kneading elements that deal with the input fibres are considered. The kneading elements at the feed zone which deal only with the polymer granules are not considered. The used kneading block is unified through all the extruder designs which is 25/5/45L (25 mm length with 5 discs left hand rotated at 45° in subsequent order). One layout (A) with 8 kneading elements and another with 4 kneading blocks (B). Screw (C) contains patented Multi-Process-Elements (MPE) which allows soft incorporation of the natural fibres into the polymer flow. The openings in the MPE element reduce the high shear forces applied on the fibres. MPE also allows the extrusion of moist wood flour/ fibres or bast fibres. The direct processing of fibres without pre-drying also eliminates any risk of explosion. The section of MPE elements was composed of right and left handed elements in order to act as a mixing element for the material flowing forward and backward.

Screw (D) with teethed blocks cause fibres cutting during entry and reversed flow which in turn helps in better fibre compounding. The different design layouts of the used extruders are shown in Figure 5-3.

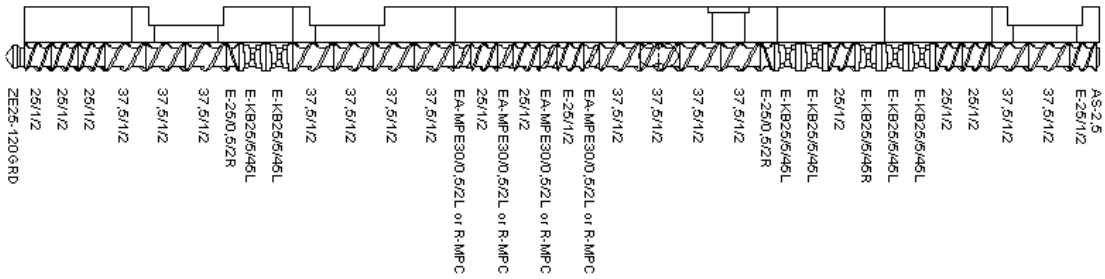
A-



B-



C-



D-

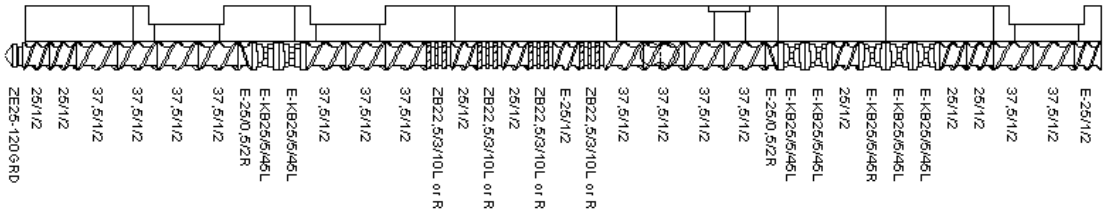


Figure 5-3: Extruders layouts of A/B/C/D

Shear rate (screw speed) effect is also carried out at 100, 200 and 300 rpm. The exit die produces two round cross-sectional composite profile which is 1:10 extrusion ratio seen in figure 3b.

The mechanical properties of the extruded NFTC will be measured in two cases:

a) As extruded without further shearing or fibre damage. The extruded strands are laid in a dog bone and then hot pressed at 500 bar and 200°C.
b) After injection moulding. The extruded strands of composites are mechanically shredded and then injection moulded. Pressed or injected samples are conditioned, tested and evaluated according to DIN EN ISO 179-1 and DIN EN ISO 527-1.

To observe the fibre geometry development along the extruder processing, the extruder is stopped during the feeding process of the fibre bundle into the extruder. The screw is then withdrawn out of the extruder housing. Then samples are taken from the fibres sticking to the screw at the positions that are directly after each element within the screw as shown in Figure 5-4. The withdrawn samples out of the extruder elements are then investigated by optic microscope as well as by the dynamic image analysis as mentioned in 3.4.3 and 3.4.4 respectively.

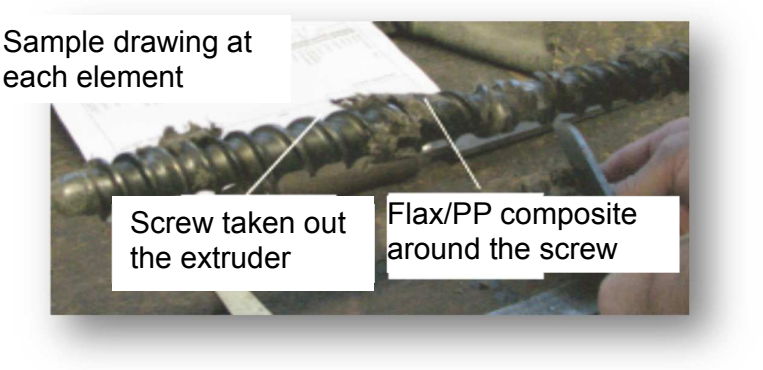


Figure 5-4: Sample taken at the end from each element after stopping the extruder and pulling the screw.

5.4 Hot pressed samples out of extruded strands

Figure 5-5 shows the tensile testing results made from hot pressing of extruded strands with respect to the fibre content for the different speeds and the different extruder configurations. It is observed that the strength of the pressed samples out of the extruded strands are less than reported from kneading in Figure 4-15. That can be attributed to adhesion problems during pressing of the extruded strands.

Generally speaking from Figure 5-5, the increase of fibre content leads to an increase in E-modulus as well as for strength as shown in Figure 5-5a and Figure 5-5b. However the configuration (A) shows a non-consistent behaviour at 20% fibre content. In case of strength, the maximum strength takes place at [20-30] wt.-% depending on the shape of the configuration and the process parameters. The reported strength values are less than that reported in literature [El-09c]. This is because the kneaded composites reach higher levels of fibre distribution and adhesion with the host matrix especially under the used high injection pressure whereas the extruded/ pressed samples have more weakness points like fibre agglomerations, lack of adhesion and incomplete mould filling during hot pressing. Table A- 2 presents the whole data of the E-modulus, tensile strength and total elongation measured for the tensile specimens.

E-modulus and tensile strength show roughly that the ranking of the extruder configurations from the lowest to the best is as follows: B-A-D-C. The strain at break is oppositely ranked where the ‘C’ configuration has the least strain and ‘B’ has the maximum strain. The reasons of the improved strength and E-modulus in configuration ‘C’ can be explained by either of the following reasons: higher fibre aspect ratio because of the soft compounding profile reached by the MPE elements, or due to more available sites on the fibre surface area and hence more free hydroxyl groups that couple with PP in occurrence of MAPP [Li07]. The share of each reason can be hereafter discussed and justified after measuring the geometry of the extracted fibres. Configuration (D) has the next performance. This is can be explained in terms of the openings within the teeth elements which play a similar role to MPE elements. However, the teethed blocks assert some damage for the fibres by shortening them mechanically and not by decohesion as preferred. This suggests that teethed block of configuration (D) is eligible for design development and hence improved mechanical results.

The other configurations (A) and (B) have lower mechanical properties in comparison with extruders (C) and (D). This implies that MPE and teethed elements play better rule in strengthening. This may be attributed to better defibrillation or better mixing by more adhesion areas. Both assumptions will be discussed in the fibre measurement section. Regarding extruders (A) and (B) with severe and light kneading, the results in Figure 5-5a and Figure 5-5b show that severe kneading leads to higher mechanical properties (in comparison with light kneading configuration). It can be depicted that the severe kneading results in more fibrillation leading to more adhesion area between PP and natural fibres and hence a better load transfer is achieved. Light kneading in configuration (B) is expected to result in larger fibre agglomerations and less adhesion area with the host PP matrix and thus less load capacity. On the other hand, the elongation at break of configuration (B) is found to be the maximum. That is because of the lower fibrillation grade in the light kneading case. Less fibrillation allows significant slide of fibre-to-fibre under mechanical loading. Also, local defects due to incomplete polymer impregnation would cause more discontinuities in fibre matrix contact which in turn allows only polymer and not fibre straining.

Figure 5-6 presents the results again but with respect to the applied speed. Except configuration (A) at 20% and 30%, there is no significant effect for speed on E-modulus as presented in Figure 5-6a. Meanwhile the effect of increasing speed on strength, Figure 5-6b, seems significant and negative especially in the speed range 100-200 rpm. Another notice is that the 30% fibre loading is the least affected by the speed change. It is also obvious in Figure 5-6a and Figure 5-6b; that the behaviour of 30% fibre loading seems superior regarding E-modulus and strength in comparison with 10% and 20% for the whole speed spectrum. 10% and 20% have overlapping behaviour along the different speeds. This suggests the non-linearity between fibre content and the measured mechanical property. The results of screw speed effect on E-modulus and strength match partially with what reported by Beaugrand [Bea13] where no significance is found for the range of 100-400 rpm.

Figure 5-6c shows the speed effect on the elongation at break. The trend appears from the first glance that it is not consistent. However, a deep insight shows that configurations (A) and (B) at 10% and 20% have an improvement trend in the range of 100-200 rpm. This suggests that there are two contradicting factors. More speed enhances the distribution of fibres homogeneously. But on the other side, the fibre length is shortened and hence the load transfer is weakened.

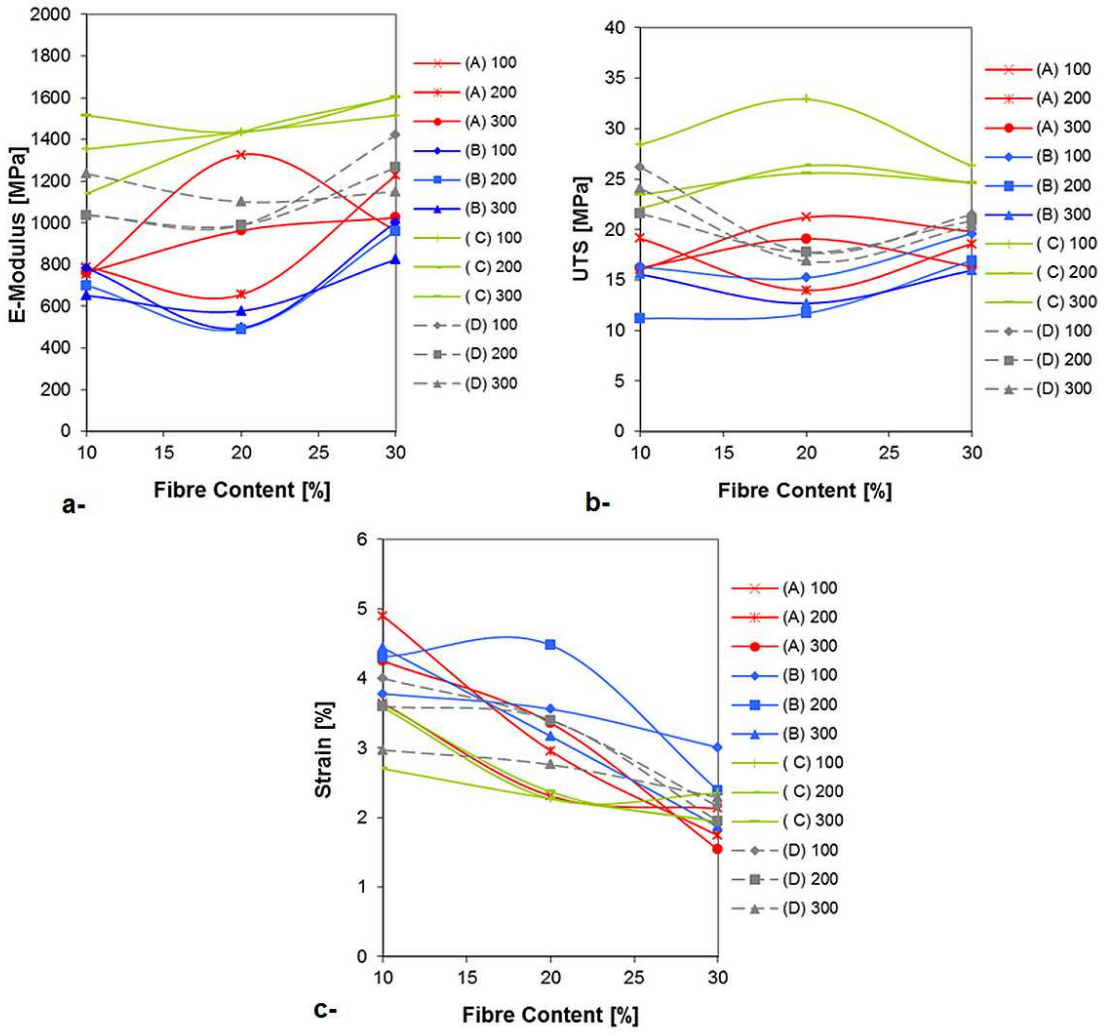


Figure 5-5: Tensile testing results with respect to fibre content a- E-modulus b- tensile strength c- Strain at break

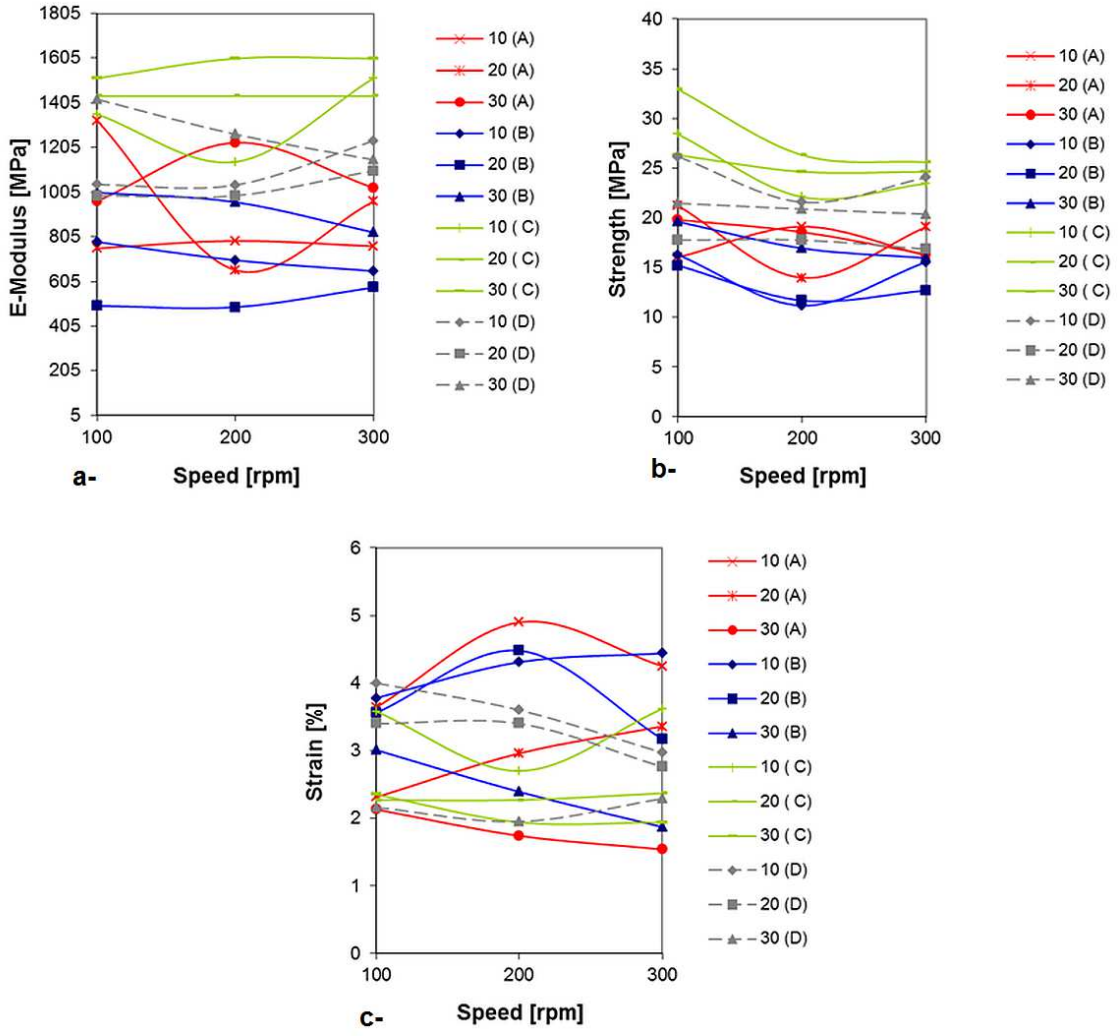


Figure 5-6: Tensile testing results with respect to speed a- E-modulus b- tensile strength c- Strain at break

Figure 5-7 shows the scaled estimates using JMP. For instance the ranking of extruder configuration with respect to E-modulus is confirmed (B-A-D-C).The extruder configuration has the largest effect on the studied properties. Fibre content has then the next large effect especially on modulus and negatively on elongation. The fibre content negative effect on elongation is even bigger than that of the extruder configuration. Speed is then the least significant on the measured properties. This analysis shows the importance of the extruder configuration because after injection moulding this effect will be reduced and remains dominantly the effect of the fibre content as shown in Figure 5-8.

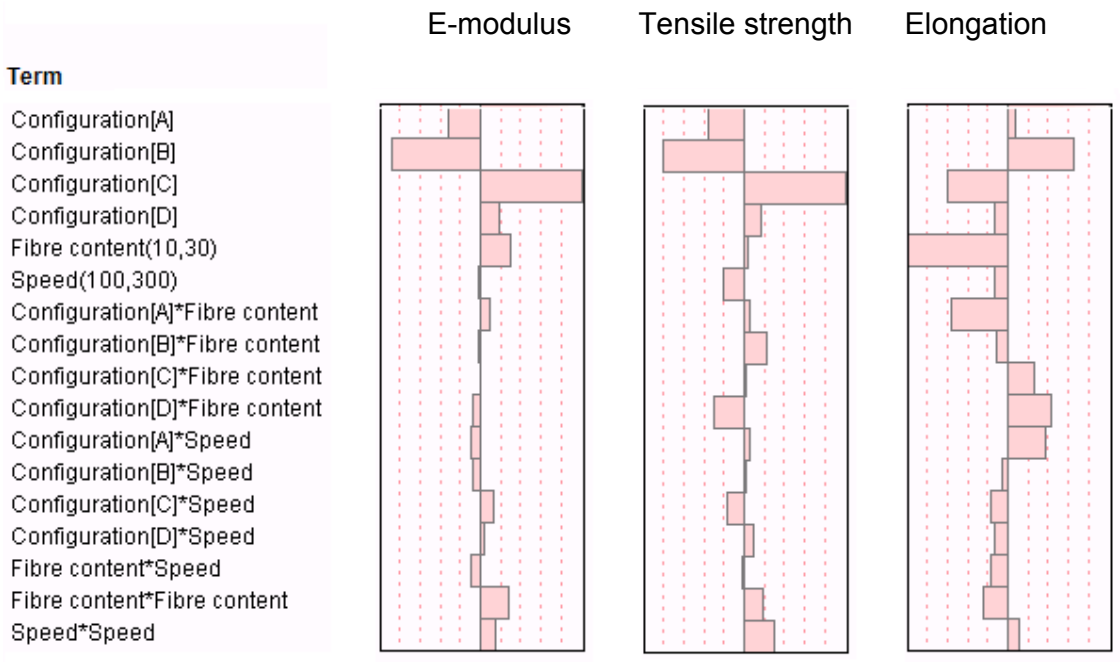


Figure 5-7: JMP analysis of scaled estimates for the hot pressed samples out of extrusion

5.5 Mechanical testing of injection moulded samples

Figure 5-8 shows the tensile strength results after the injection moulding with respect to the fibre content for the different extruder configurations. This time, the effect of fibre content is more significant in comparison to the behaviour shown in Figure 5-5. This means that the effect of extruder configuration is getting smaller especially with the low fibre content 19%. Configurations (A) and (B) show linear improvement with steep increasing gradient with respect to fibre content. This can be attributed to their weak strength nature in the pressed/ extruded case. Therefore just further hot shearing during injection moulding process has induced this improvement. On the other side, configurations (C) and (D) did not show such improvement with low shearing rate at 100 rpm. This behaviour suggests that the fibre geometry and distribution was already good in the first processing phase (extrusion) so that no significant improvement is observed after injection moulding. This infers that fibre aspects did not alter significantly after injection moulding after extrusion at shear rate of 100 rpm. It is also obvious that at 30% fibre content; the effect of speed is totally insignificant for configurations (A) and (B) where all speeds' curves coincide together as enclosed in the shown circles. This may be attributed to the reached level of severe fibre damage due to excessive friction in 30% fibre content by configurations (A) and (B). Whereas the configurations (C) and (D) show that there is a difference between strengths of the composites reinforced with 30% fibre at the different applied speeds.

Figure 5-8b shows the improvement ratio of the tensile strength by dividing the injection moulded strength to the strength of the pressed strands. The improvement is maximized in case of the configurations (A) and (B) and minimum by configuration (C).

Configuration (D) improvement level lies between those of configurations (C) and (A). The improvement is in all cases positive (>100%) which implies the enhancement of the adhesion between fibre and polypropylene and the distribution pattern of the natural fibres in the polypropylene matrix. But from another way, the minimum improvement of configuration (C) suggests that the required mechanical properties can be reached by extrusion without the need to further processes. In other words, energy consumption can be attained by selecting suitable configuration of the twin screw extruder.

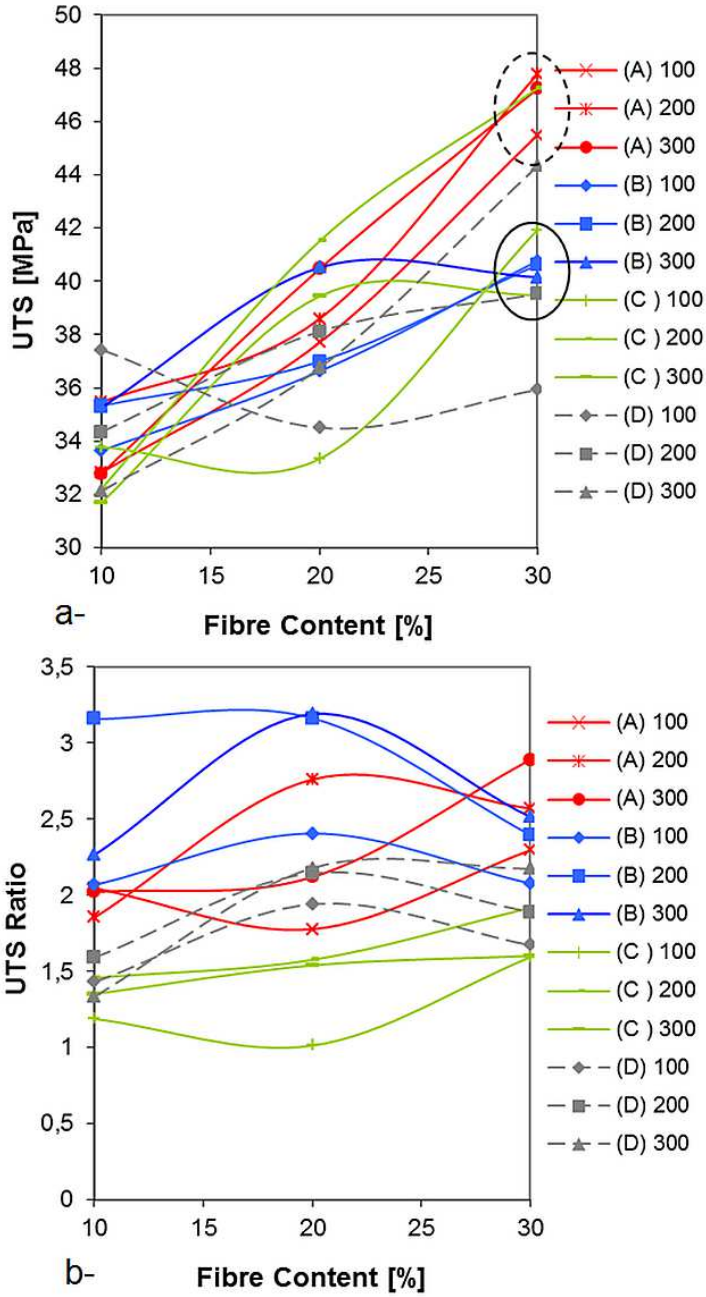


Figure 5-8: Tensile testing results after injection moulding a- tensile strength of injected samples b- Tensile strength ratio of injected to extruded samples

5.6 Effect of extruder configuration on the fibre length/ diameter

As mentioned in 3.4.4, the extruder is stopped during running at 30% fibre content and 200 rpm conditions for the characterisation of fibre size (length and diameter) and its effect on the mechanical properties. The extruder is drawn from the machine body and samples are taken after each element. Samples are dissolved. Fibres are extracted and measured using Qicpic. lists the diameter and length of the fibres at 3 cumulative levels namely 10%, 50% and 90%. Fibre diameter decreases slightly from one element to another. This is interpreted earlier by the effect of the extruder configuration on the fibre diameter either due to the quick fibrillation or due to the huge amount of elementary fibres which are considered in the statistical calculation. Therefore focus will be asserted on the fibre length and its development. The convergence of the fibre distribution is represented by the quotient (X90/X10) where the fibre convergence is becoming better when this quotient is getting decreased. Table A- 3 presents the results of this quotient as well as the aspect ratio.

Table A- 3 shows numerically the effect of the element type. In extruder ‘A’, the fibre length at 50% accumulative density function decreases gradually. A fluctuation in fibre length takes place at the end of the kneading phase (position E and F) where the length increased. This fluctuation is attributed to the new short fibres appearing (they are too many however they are underestimated or disregarded when their lengths are less than a user-defined value of 100 µm). Underestimation of fibres is attributed to the use of Q2 statistical evaluation where long fibres have more weight in calculation as mentioned in section 2.1.1.

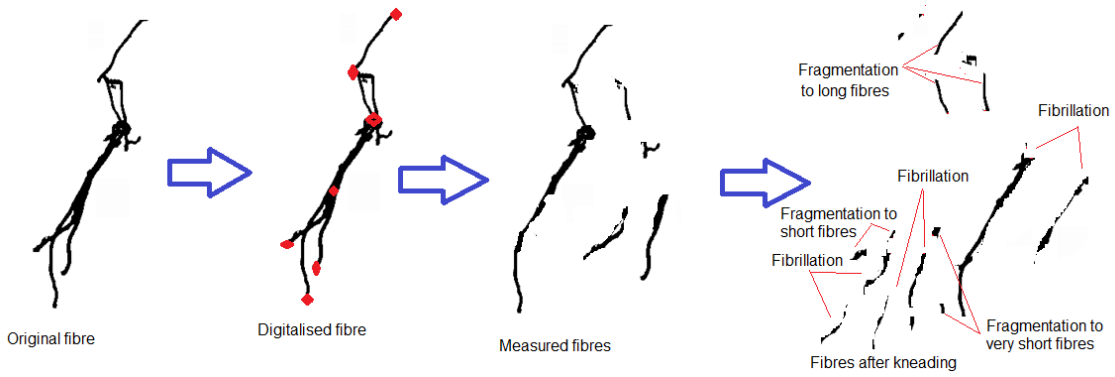


Figure 5-9: Measurement and development of flax fibre by QICPIC system

After that, drop in fibre length is obvious along the transport element due to temperature and shearing (see the difference in readings of X50 between the last two positions 473,3 and 646,0 mm). In extruder ‘B’, the reduction, no fluctuation or big drop is observed after the kneading phase. This is attributed to the few kneading elements

in comparison with the doubled number of kneading elements in extruder ‘A’. A drop in fibre length is observed again along the transport elements (see the difference between positions D and E, 293.3 and 400 mm respectively. In extruder ‘C’, a smooth reduction in fibre length is observed. While in extruder ‘D’, a drop is observed in the fibre length after the first and the second teeth block elements. After that, stability in behaviour is observed.

Figure 5-10 shows the development of the aspect ratio for all extruders. It is clear that aspect ratio reduces along the extruder in general but extruder ‘C’ preserves a stable behaviour of AR. Also extruder ‘A’ where more kneading elements exist, shows high AR at the beginning as a better fibrillation is reached (see that X90/X10 is more homogeneous and small for ‘A’ in comparison with ‘B’). Also it is worth to note that the aspect ratio of extruder ‘D’ is always less than those of the others especially at the beginning. This presents the effect of the teeth elements where fibres are cut mechanically and not only due to decohesion of fibres under temperature and shearing.

Figure 5-11 shows X90/X10, regarding fibre length only, to check the homogeneity of the fibre length distribution along the extruder length. The quotient is reduced to one third indicating homogeneity in the distribution and more convergence. From both Figure 5-10 and Figure 5-11, it is obvious that stability of AR and X90/X10 is reached in case of extruders ‘C’ and ‘D’ after short extrusion length without much need to the kneading elements phase. This suggests the possibility of using extruders with lower L/D ratio.

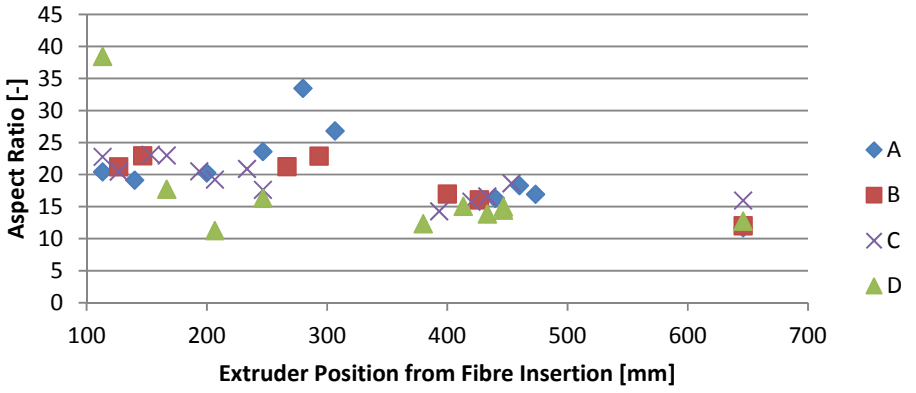


Figure 5-10: Fibre aspect ratio along the different extruders at 30% Wf and 200 rpm

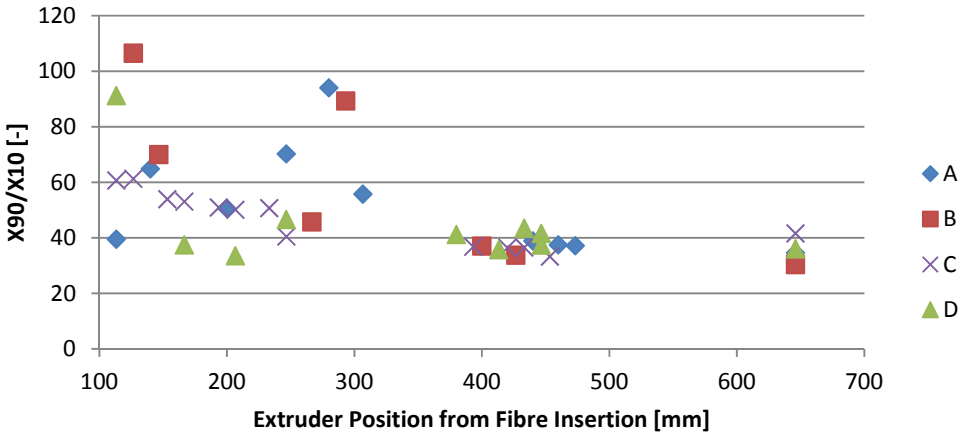


Figure 5-11: X90/X10 quotient (regarding fibre length) along the different extruders at 30% Wf and 200 rpm

The data from the all elements at all extruders are collected and a Weibull distribution is selected [And06] to describe the behaviour of fibre length. The probability density function of Weibull distribution is given in Equation 5-4 where 'a' and 'b' are the scale and shape factors respectively.

$$f(x) = b\frac{x^{b-1}}{a^{b}}e^{-\left(\frac{x}{a}\right)^{b}}$$

Equation 5-4

Using fitting tools of MATLAB, the Weibull parameters are calculated for the measured fibre length distributions. The 'a' and 'b' parameters are used again to plot the hypothetical Weibull density functions along the extruder length as shown in Figure 5-12, Figure 5-13, Figure 5-14 and Figure 5-15. These distributions can help in modelling the fibre length and the effect of the extruding elements. Figure 5-12 shows the Weibull curves of extruder 'A'. The median of the fibre length decreases along the extruder from point A to C (the curve shifts to the left). But at point F, the curve becomes wider and shifts to right. This indicates that the aggressive kneading imparts different modes of fibrillation and fibre fragmentation. After the last kneading positions, at positions (H, I), the curve shifts again to the left with narrower distribution.

The behaviour is interesting in extruder 'B' shown in Figure 5-13. The Weibull curve is too wide at position A (before kneading) indicating wide spectrum of deviation. At the first kneading element, the wide deviation starts to get narrower and the median shifts to left. Then after a relatively long transport by the transport elements and passing another kneading pass, the bell form of the curves are remarkable and the curve

medians shift more to the left. This suggests that the fibrillation is affected also by the high temperature along the extrusion even without the presence of kneading elements.

The most smooth transitional behaviour is shown in extruder ‘C’ using MPE elements, Figure 5-14, where the curve medians shift gradually to the left firstly by the MPE element and then more remarkably by kneading elements. The behaviour is slightly different in extruder ‘D’ shown in Figure 5-15, where the mechanically cut fibres show a flat plateau at the beginning and then great convergence after kneading. This can be thoroughly seen where the quotient X90/X10 values reduced drastically from 91 before the first element to almost 30 starting from the second element.

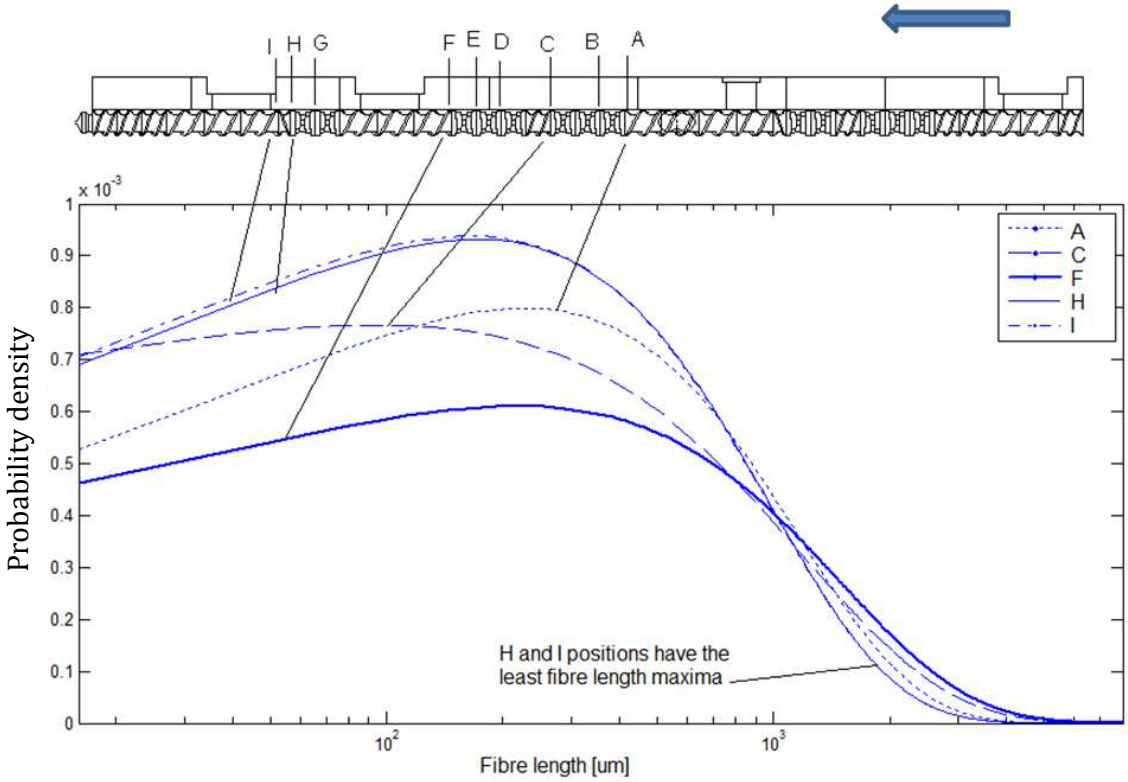


Figure 5-12: Weibull distribution of the fibre length along the extruder ‘A’ at 30% Wf and 200 rpm

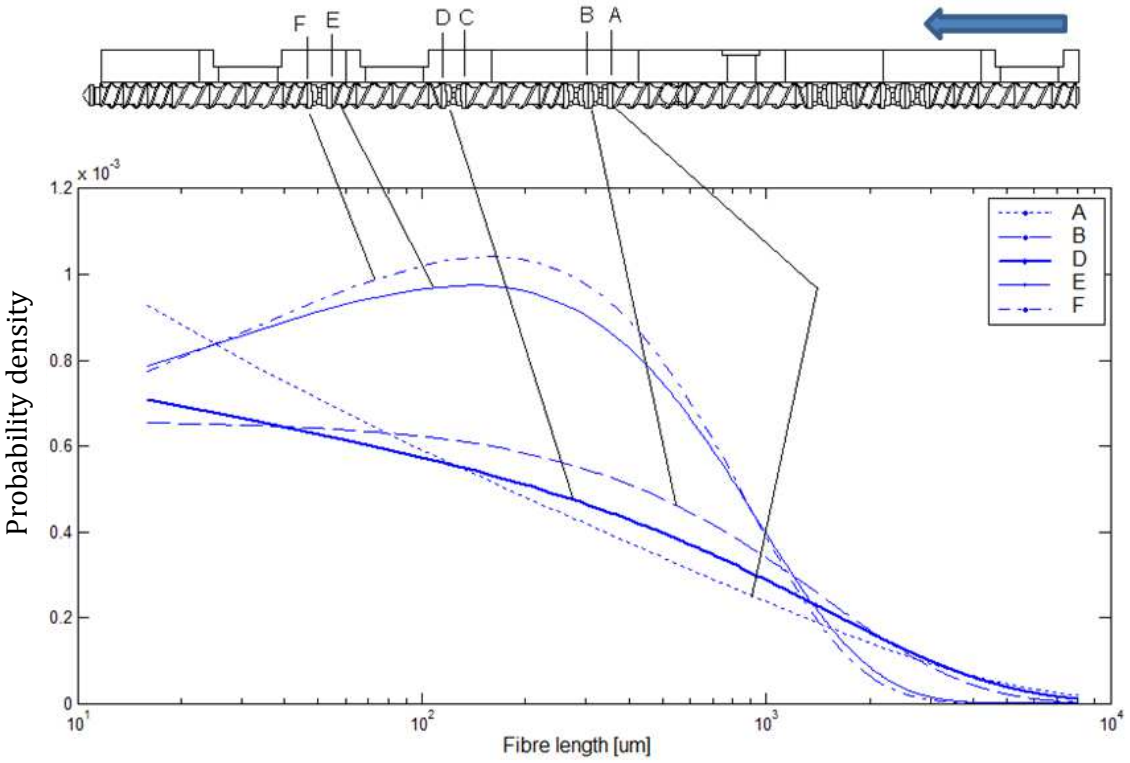


Figure 5-13: Weibull distribution of the fibre length along the extruder 'B' at 30% Wf and 200 rpm

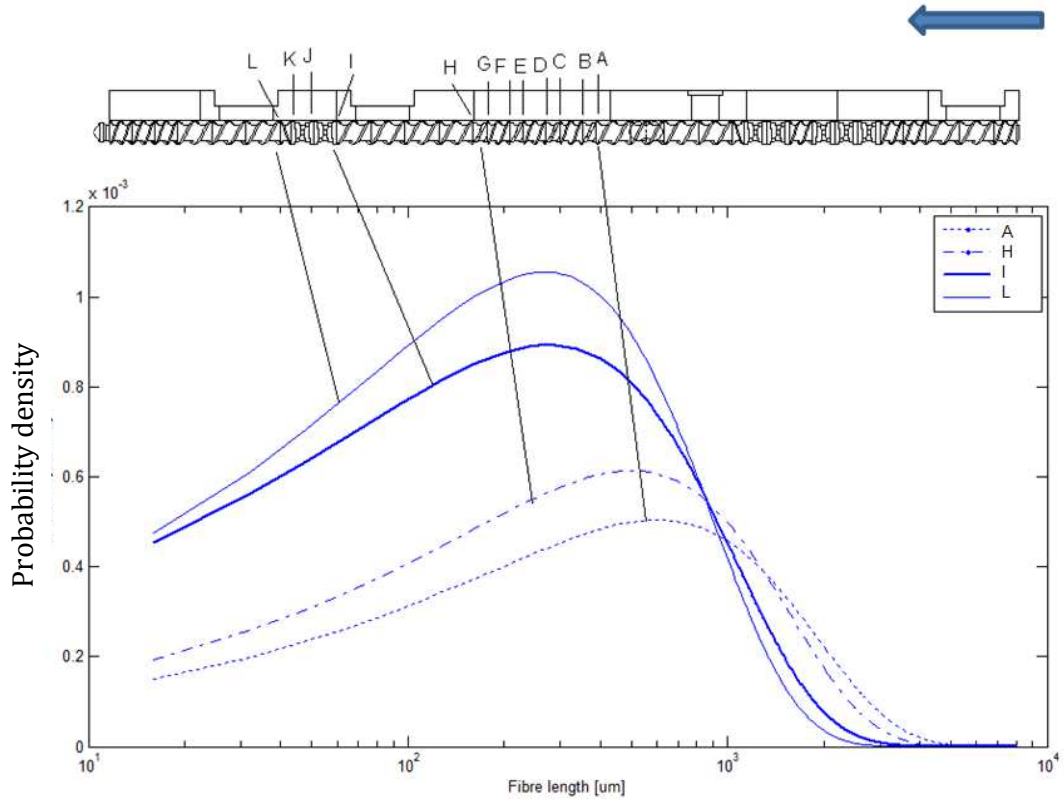


Figure 5-14: Weibull distribution of the fibre length along the extruder 'C' at 30% Wf and 200 rpm

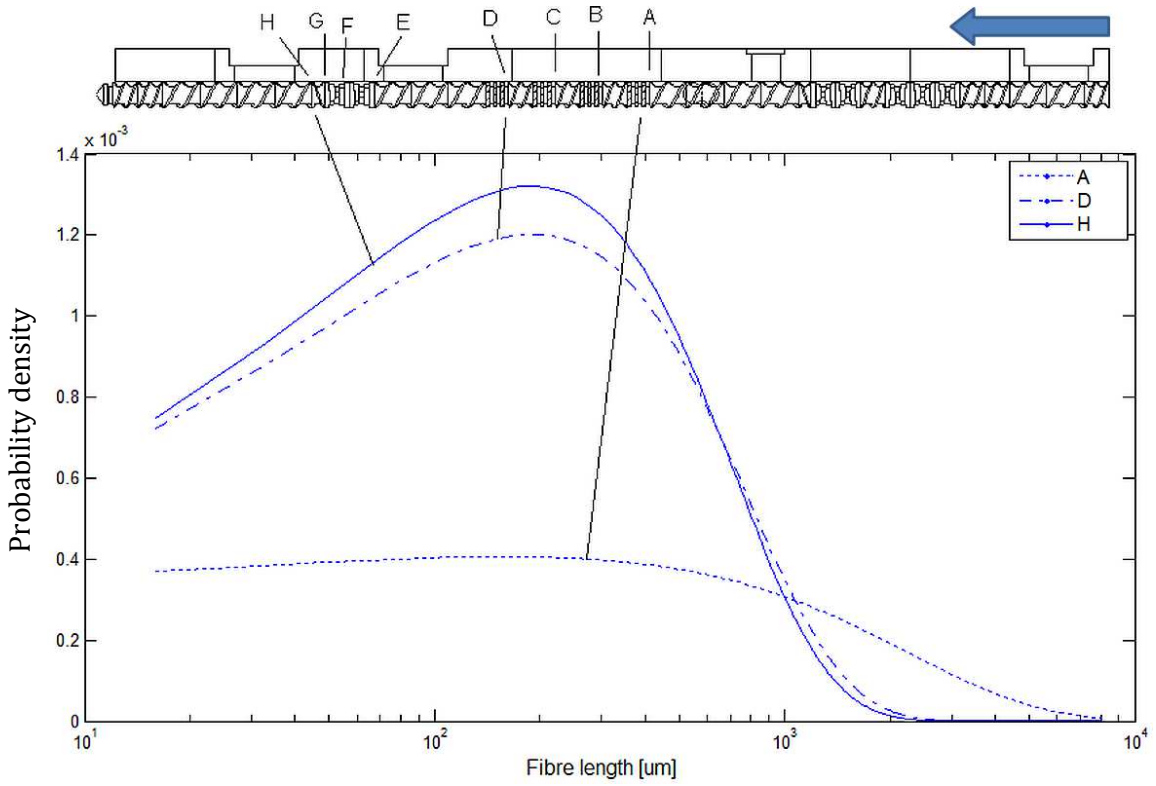


Figure 5-15: Weibull distribution of the fibre length along the extruder 'D' at 30% Wf and 200 rpm

5.7 Outcomes

The effect of the extruder configuration and the processing parameters on the PP/ Flax composites can be concluded in the following aspects regarding:

- The ranking of extruder configurations from the lowest mechanical properties to the best is as follows: B-A-D-C as in the example shown in Figure 5-16 for 20% fibre content and 200 rpm. The strain at break is oppositely ranked. The improvement in E-modulus and tensile strength is attributed to either of the following reasons: higher fibre aspect ratio, or due to more available sites on the fibre surface area to couple the polymer with the natural fibre. The fibre measurement supported the second reason.
- Effect of extruder configuration is substantial but it then decreases after injection moulding. Fibre content has also a significant effect on the measured mechanical properties and then the speed which has the least effect as it affects the fibre distribution within the matrix.
- The stability of AR and X90/X10 is reached in case of extruders 'C' and 'D' after short extrusion length without much need to the kneading elements phase. This suggests the possibility of using extruders with lower L/D ratio.

- Definition of the Weibull distribution parameters is helpful in the modelling of the fibre size along and after the extrusion which can be then correlated to the expected mechanical properties.

As a summary, this work shows the effect of the extruder configurations on the attained properties. This work proves also that the common idea of increasing strength along with the increase of the aspect ratio is not only the key player in the overall composite behaviour. Aspect ratio develops along the different elements on the extruder even with the presence of almost low shearing transport elements. This depicts that there are other factors like fibre decohesion (defibrillation which imparts the formation of greater surface area) attributed to the induced temperature which influences the resulting fibre geometry.

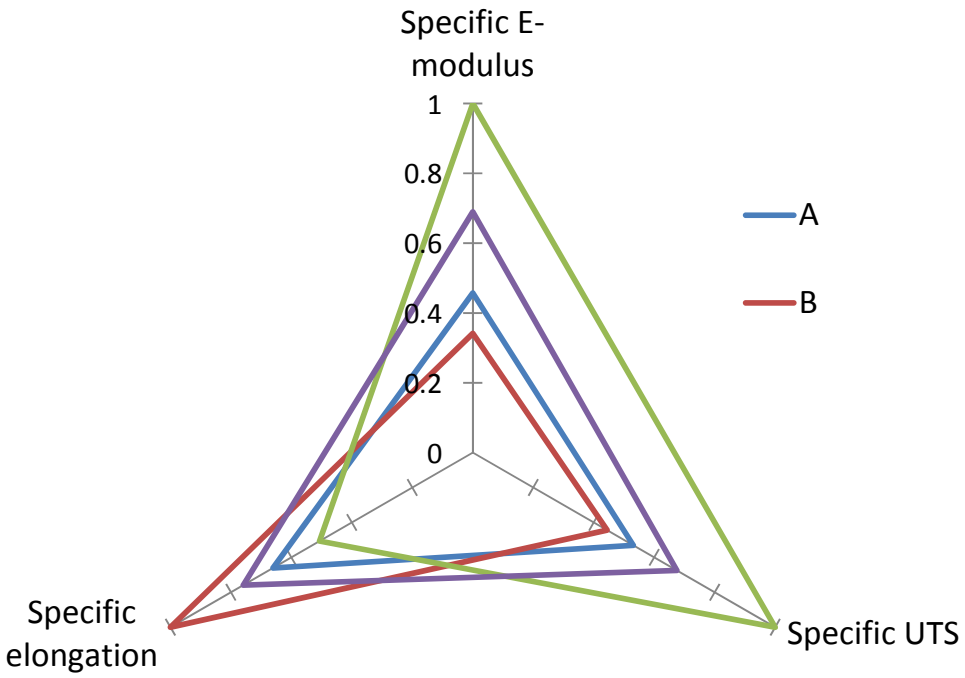


Figure 5-16: Effect of extruder configuration on the E-modulus, strength and elongation of 20 wt% fibre content and 200 rpm

6 Optimising the injection moulding parameters

6.1 Optimisation concept of the injection moulding parameters regarding mechanical properties

6.1.1 Introduction

The effect of injection moulding parameters on the mechanical properties of the injection moulded thermoplastics is already proved and reported in the literature [Xie09], [Kul10], [Ota05], [Ber00], [Kub74], [Lal13], [Has13], [Gra14]. The optimisation studies are different in which parameters are taken into consideration. Some data about the literature of optimisation as follows are:

- Hassan [Has13] worked on polystyrene (PS) and low density polyethylene (LDPE) studying the parameters of (packing time, packing pressure, injection pressure, injection time, ejection time, injection velocity, cooling time). It was found that the most important factors, in a descending order, are packing pressure, injection pressure and then the packing time). Packing pressure, where additional melt is fed to compensate the shrinking polymer in the filling stage, controls to a great extent the final mechanical as well as physical properties such as (birefringence, residual stresses, density distributions, and product shrinkage and warpage) [Hua99]. However, there are no data about the range of investigation for the cooling time and temperature in [Has13]. Also the statistical techniques for the design of experiments are not followed to estimate the significance of each factor, even the mechanical properties are not used as response decisive factor for the resulting final evaluation.
- Bernhardsson [Ber00] studied the hot press moulding technique (pressure, temperature and time) on PP/GF. The measured response is the composite strength. The experimental plan considers the quadratic effect (the effect of one factor is not constant but depends on the value taken by another factor). Therefore the factors are (pressure, temperature, time, pressure*pressure, temperature*temperature, time*time, pressure*temperature, temperature*time, time/pressure). The most significant factors were found to be ranked as follows starting by the most positive factor: Temperature, time and then the applied pressure. Significance of the interaction effect of time with pressure and temperature is also proved. However these interactions have negative effect on the response strength.
- Lal [Lal13] used the Taguchi method to study the effect of melting temperature, injection pressure, refilling pressure (pack or post pressure) and cooling time on the shrinkage of LDPE. Signal-to-noise ratio (S/N) instrument, which reflects both the average and the variation of the quality, is followed. Shrinkage and not the mechanical property is the response, to be minimised, in this study. The results showed that the cooling time was the most significant factor followed by the pack pressure, melting temperature and injection pressure was found to be the least effective factor. It is interesting here to note that the optimum

combination of processing parameters is the least temperature and pressure, while the cooling time as well as the packing pressure were maximised.

- Lei [Xie09] used again Taguchi method but in the micro-injection of PP. The studied parameters are Melt temperature (210, 230, 250°C), mould temperature (120, 140, 160°C), injection pressure (500, 1000, 2000 MPa), packing pressure (400, 800, 1600 MPa), ejection temperature (40, 60, 80°C) and injection speed (60, 80, 100 cm^3/s). The response, to be maximised, in this study is the ultimate tensile strength of the weld line containing V notch profile. The significance order of the processing parameters regarding the weld line strength descendingly is: Mould temperature, melt temperature, injection speed, ejection temperature, packing pressure and the least significant factor is the injection pressure. The influence of mould temperature is very significant here because it is higher than the crystallisation temperature of PP which is normally around 120°C. Lower than this temperature, incomplete filling problem occurs. While more than 120°C, filling is complete but the cooling till the demoulding temperature (less than the crystallisation temperature) induces more shrinkage especially when the phase transformation takes place at 120°C and no more PP is available to substitute shrinkage (post filling step is already finished). Generally, it is found that only the first factors are worthy to be considered and the other two factors, related to pressure, are insignificant. The optimum processing parameters are found by combining the S/N ratio analysis and the extreme error analysis. Similar to [Lal13], melt temperature and injection pressure are minimised to maximise the mechanical properties.

As seen from the previous introduction, the main significant factors that affect the injection moulded products are the temperature related factors like melt and mould temperatures as well as cooling time. The significance of other factors like injection speed, pressure and filling pressures are controversial and changing from one literature to another and depending on one response function to another (strength, shrinkage…).

The motivation to this section of work is to optimise the injection moulding parameters in order to maximise the mechanical properties. In order to avoid as much as possible the inhomogeneity of properties suffered in non-industrial scale production, the selected NFTC for experimentation in this study is a commercial product. FiberGran F 25 is a commercial granules supply which consists of 25% flax fibre and 75% PP characterised with good flowability, aging resistant and thermal stability properties as mentioned in Table 3-1.

6.1.2 Plan of work

JMP® 10.0.0 is used to design the experiments. The responses are the mechanical properties (E-modulus, tensile strength and impact strength of un-notched Charpy samples). The objective is to maximise the mechanical properties. The factors investigated are:

- Injection pressure: continuous type from 500 to 1000 bar.
- Temperature of the polymer melt: continuous type ranging between 180 to 200°C (Nozzle temperature out of the injection machine).
- Temperature of the injection mould: continuous type ranging from room temperature (25°C) to 80°C
- Screw velocity: continuous type ranging from 20 to 40 m/min.

Using standard design with a two-factors interaction, a plan of experiments is designed as shown in Table 6-1. Cooling time is not considered in this study, although it was the most significant factor in [Lal13] when this time is extended. The reason is that the industry does not prefer the methods negatively affecting the production cycle time.

Spirals are injection moulded with Arburg 320 C600-250 and evaluated regarding the flowability as mentioned in Figure 3-3. The tensile samples of 1BB size are injected according to DIN EN ISO 527-2.

Table 6-1. Experimental plan of NFTC injection moulding optimisation

Sample #	Temperature [°C]	Pressure [bar]	Mould temperature [°C]	Screw speed [m/min]
1	180	500	25	20
2	180	500	25	40
3	180	500	80	20
4	180	500	80	40
5	180	750	80	32
6	180	1000	25	30
7	180	1000	52,5	40
8	180	1000	80	20
9	190	500	52,5	30
10	190	1000	25	20
11	190	1000	80	40
12	192	750	80	20
13	200	500	25	20
14	200	500	25	40
15	200	500	80	20
16	200	500	80	40
17	200	750	58	40
18	200	1000	25	40

19	200	1000	52,5	20
20	200	1000	80	30

6.1.3 Results and discussion

Table A- 4 presents the mechanical properties of the samples mentioned in the experimental plan of 6.1.2. The scaled estimates of the results, constructed using JMP software, are shown in Figure 6-1. Significance is proved for all factors out of the blue lines in the ranking of mould temperature, temperature and temperature interactions with temperature, mould temperature and pressure. This matches with the previous findings [Ber00] that the temperatures (polymer and mould) are the most significant while the pressure has the least significance.

To summarise the interactive effect of the studied parameters, a prediction profiler out of these results as shown in Figure 6-2. The optimum results (E-modulus of 2193 MPa, tensile strength of 30.8 MPa and impact strength of 11.8 kJ/m²) with respect to the mechanical properties are 181°C, 500 bar, 80°C and 20 m/min for temperature, pressure, mould temperature and screw speed respectively.

These optimum results are average performance results and cannot be generalised for each single response (E-modulus, tensile, impact). Trend lines of screw speed in Figure 6-2 shows insignificance as presented Figure 6-1. However the other factors show different effects on the response properties. For example, the increase of the temperature (polymer and mould) improves the E-modulus but on the other side decreases the impact strength and vice versa in case of pressure effect. Tensile strength behaves almost like E-modulus but in relatively lower trends. It is worthy to note that if the response is else like the spiral flow length, different results will be obtained.

6.1.4 Outcomes

The results matched the previous reports [Xie09], [Lal13] that low temperature and pressure as well as high mould temperature increase the mechanical properties of the NFTC samples. In case of PP natural fibre composites, 180-185°C, 500 bar, 80°C and 20 m/min for temperature, pressure, mould temperature and screw speed respectively are optimum results when the mechanical properties are only considered.

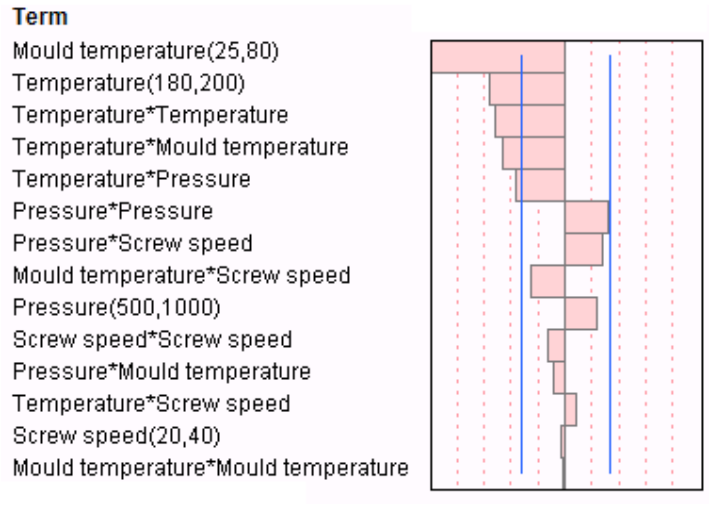


Figure 6-1: JMP analysis of scaled estimates for the injection moulded NFTC samples.

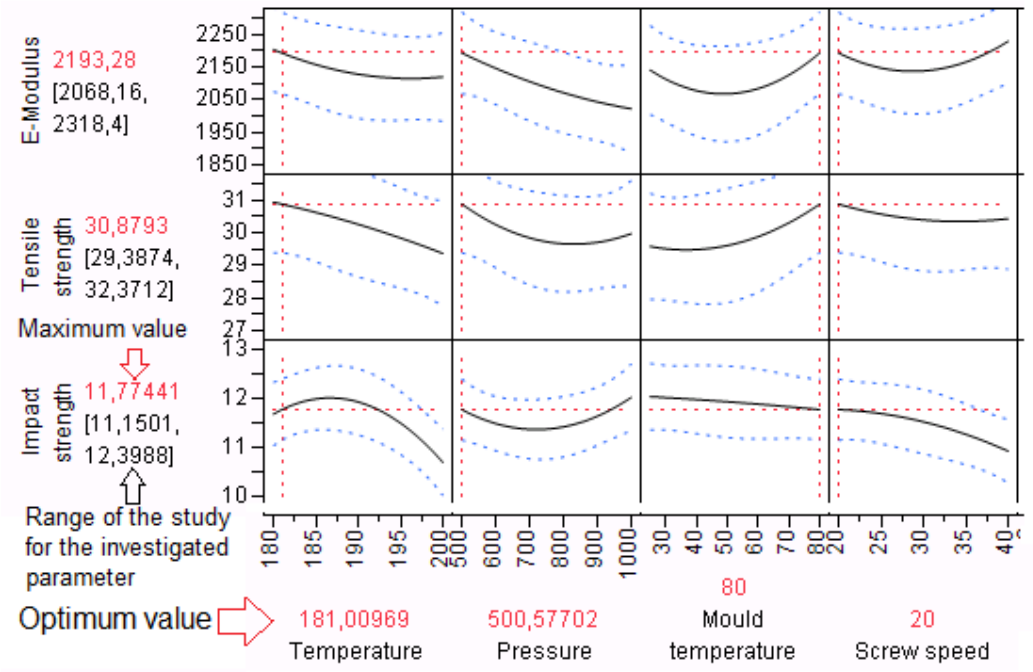


Figure 6-2: Prediction profiler regarding the mechanical properties

6.2 Study of Injection Moulding Parameters (Mechanical/ Flowability/ Modelling)

6.2.1 Introduction

Natural fibre reinforced polypropylene composite (NF/PP) represents a great share of the injection moulded NFTC in Europe. NF/PP composites represent 92% of the 15000 ton of the total production volume of NFTC [Dam13]. It is reported that the fibre content fluctuates strongly in comparison to the nominal fibre content [Fin14], [El-14a], [El-13a], [El-13b]. Accordingly, a product with uneven mechanical and shrinkage properties is produced. Such problems of uncertain mechanical properties or warped products will affect negatively on both the production efficiency and the product cost.
According to literature, this change in fibre content points to phase separation phenomenon. It takes place between the reinforcing fibres and the polymer melt at the stage of entering the mould [El-13b]. This is attributed to the differences in the densities between the matrix and the fibres as well as to the shape of the fibres (straight / branched). Kubat et al. [Kub74] reported the same phenomenon in spiral mould injection of low density polyethylene (LDPE) reinforced with 25.7% glass fibres. Kubat [Kub74] found that the phase separation increases with the increase of both the injected spiral length and the viscosity. The change of the glass fibre content was found to decrease just after the injection point before it increases again along the spiral length. Helger et al. [Heg85] carried out experiments on filler homogeneity of injected dumb-bell specimens with different geometries processing parameters. Different sizes of glass fibres and glass beads are used. It was found that the significant factors are the geometry of both filler and the mould. Temperature, injection time, filler content and polymer material are coming next in significance [Heg85]. Helger [Heg85] tried to interpret the phase separation by the inertia and the normal stress effect on fillers. Thus lead to the perpendicular flow of fibres to the main injection direction and hence more filler content near to the axis. This migration towards the higher speed fluid results consequently in the higher filler content at the far end of the injection moulded samples.

The study of Peltola et al. [Pel11] was the first in considering the phenomenon of changing fibre content, qualitatively, in case of natural fibres namely hemp and flax. However this study contains a quantitative analysis of fibre length distribution in the injected dumb-bell specimens. Effects of processing melt viscosity and fibre type effects on the fibre length were investigated. Processing as expected reduced the fibre length. A reduction of fibre length along the increasing fibre content was also detected. This reduction is attributed to the increasing shear forces during compounding. Hemp fibres preserve higher aspect ratio, hence higher reinforcing, due to its fibrillation compared to flax. Ramzy et al. [Ram14] studied the flowability and fibre homogeneity of NFTC using hemp and sisal in spiral injection moulds. Polymer temperature, mould temperature and injection pressure have positive effect on the measured spiral length. The fibre content, similar to [Kub74], along the spiral shows again this decrease after the injection and then the increase in fibre content. The fluctuation in sisal was less than that measured in hemp because of the agglomeration encountered by hemp.

This work is studying the flowability and fibre content homogeneity comprehensively with different types of fibres (natural fibre such as hemp, flax, wheat straw, sisal, kenaf, wood fibre versus man made regenerated celluloses), different fibre contents (10-30%), different fibre lengths (0.5-1.5 mm) and different natural fibre shapes (branched like hemp and flax versus non-branched like cellulose sisal).

6.2.2 Strategy of experiments

The materials under investigation are listed in Table 3-1. The host matrix is a high flow PP of trade name Moplen EP 500 V developed by LyondellBasell Industries. Hemp, flax, kenaf pellets are supplied from BaVe Badische Faserveredelung GmbH, Malsch, Germany but the corresponding composites are extruded at Hannover. Sisal product is compounded in Voerde, Germany while wood fiber composite is from Rettenmeier. Regenerated celluloses are supplied by Cordenka.

Table 6-2 lists the fibre content and the characteristics of the used natural fibres in this section. Compounds are injected at different processing parameters to see their effects on the flowability of the NF/PP and the fibre content distribution along a spiral injection mould as shown in Figure 3-3. Table 6-3 shows the investigated parameters whether processing (injection temperature, mould temperature and injection pressure) or material properties (fibre type, fibre content, fibre length and fibre shape).

Table 6-2. Compounds and original natural fibre data

sample #	Fibre	Fibre content [wt.-%]
1	Cellulose (length = 0.5mm)*	10
2	Cellulose (length = 0,5mm)*	30
3	Cellulose (length = 1,5mm)*	30
4	Hemp Pellets	30
5	Flax Pellets	30
6	Sisal	30
7	Wheat straw	30
8	Kenaf	30
9	Wood fibre	30

*1.8 dtex / 12.4 µm

After injection of 15 samples for each condition, the spiral lengths are measured to evaluate the flowability. To evaluate the fibre distribution; small portion is cut from the injection part and every 10 cm further in order to extract fibres. Hence, the distribution quality of fibre the content along the spiral is estimated. Fibres are extracted by Decalin [Ram14] and the results are then treated statistically using JMP software.

Table 6-3. Experimental plan for flowability and fibre content

Injection temperature [°C]	Mould temperature [°C]	Injection pressure [bar]	Compounds*
180	25	500	2, **3, 4**, 8, 9
180	25	1000	**2, 3, 4**, 8, 9
180	80	500	2, **3, 4**, 8, 9
180	80	1000	**2, 3, 4**, 8, 9
200	25	500	**2, 3, 4**, 8, 9
200	25	1000	**2, 3, 4**, 8, 9
200	80	500	**1, 2,** 3**, 4**, 5, 6, 7, 8, 9
200	80	1000	**1, 2, 3, 4**, 5, 6, 7, 8, 9
220	25	500	**2, 3, 4**, 8, 9
220	25	1000	**2, 3, 4**, 8, 9
220	80	500	**2, 3, 4**, 8, 9
220	80	1000	**2, 3, 4**, 8, 9

*Samples are estimated for flowability and bold samples are characterized additionally for fibre content

6.2.3 Correlation aspects

Experimental spiral length is shown in Figure 6-3a to illustrate the effect of pressure. The relatively shorter flow length of the cellulosic composites group in comparison to the other fibres is attributed to their higher viscosity. By doubling the pressure, the flow length increases with 20-30% depending on the mould temperature. The effect of increasing the melt temperature from 180°C up to 220°C is shown in Figure 6-3b. The spiral length is increased by 45-55% according to the used injection pressure. This is attributed to the decrease in viscosity of the PP polymer by increasing the temperature [Ram14].

Pressure parameter was found to be the most significant parameter on the results as presented in the scaled estimates of Figure 6-3c. Increase of fibre content from 10 to 30% in cellulose decreases the flowability remarkably while tripling the fibre length seems not to be significant as shown in Figure 6-3a. Also, the branched bast fibres like hemp and flax have relatively less flowability in comparison to the non-branched with higher flexural strength fibres such as sisal, wood fibre, wheat straw and cellulose.

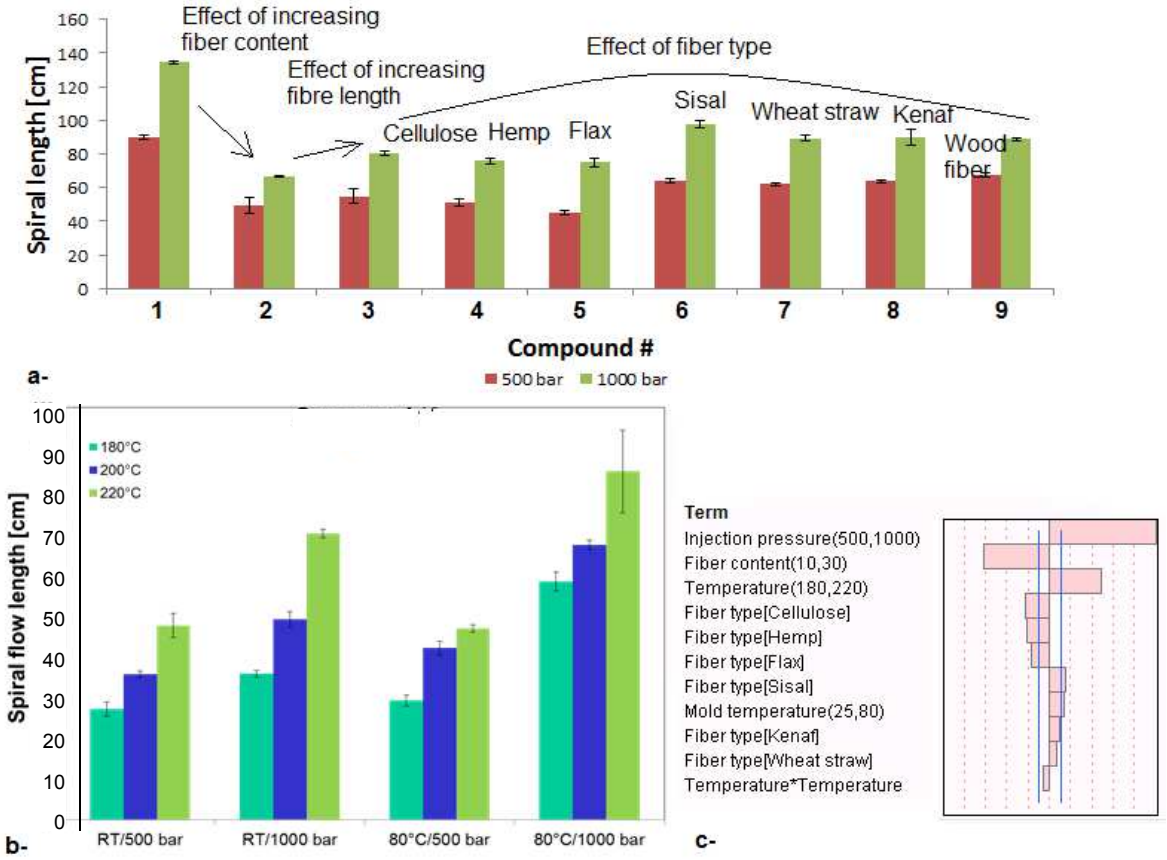


Figure 6-3: Flowability test a- Effect of fiber type b-Effect of temperature/ mould temperature c- scaled estimates using JMP

As obvious in Figure 6-4, the significant factors besides to fibre content and its interaction with pressure for both cellulose and hemp are: pressure, temperature. Mould temperature was only significant in hemp case.

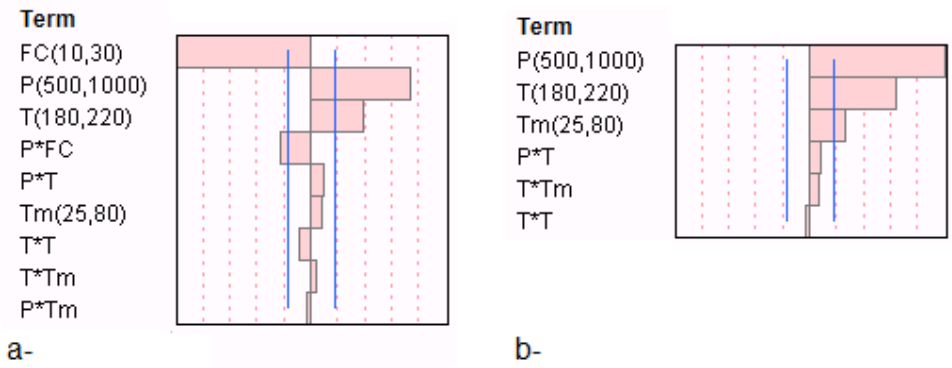


Figure 6-4: Scaled estimates of the flowability test for PP/NF composites a- Cellulose b-Hemp

The fibre content is measured along the spiral length and plotted in Figure 6-5 for compounds 3 and 4 to represent the regenerated (synthesized) cellulosic group composites against the natural (non-synthesized) fibre composites. The spiral length is measured for the two cases of mould temperature (room temperature and 80°C). As

shown in Figure 6-5a and Figure 6-5c, the fibre content fluctuation in case of compound 3 is less than that of compound 4. This is explained by the fibre tangling. Regenerated cellulose of compound 3 has higher cellulose content. Hence, higher crystallinity and higher flexural strength are attained [Sat82] so it is unlikely for compound 3 to get tangled.

The results of fibre content distribution are represented in Figure 6-5 in terms of the change in fibre content (VariationFC)as shown in Equation 6-1. Similarly, the change of fibre length (VariationFL) measured by dynamic image analysis is represented in percentage, as in Equation 6-2 to follow the change of fibre length as a function of change in fibre content.

$$Variation_{FC} = \frac{FC - FC_{average}}{FC_{average}} * 100$$

Equation 6-1

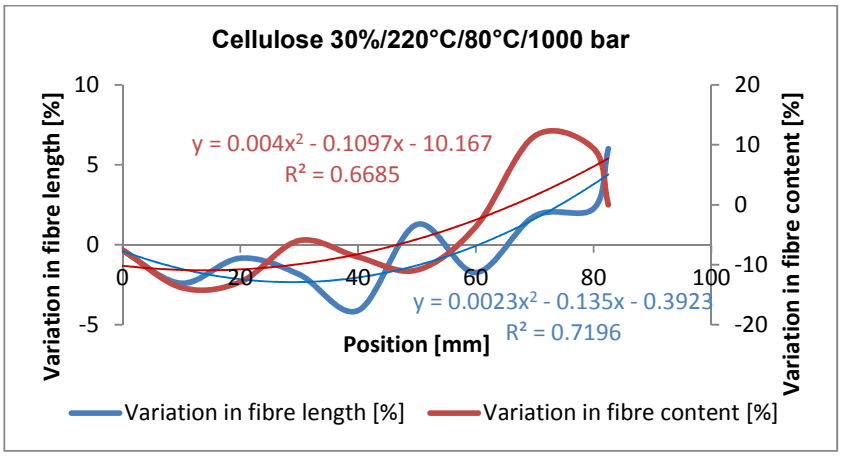
$$Variation_{FL} = \frac{FL - FL_{average}}{FL_{average}} * 100$$

Equation 6-2

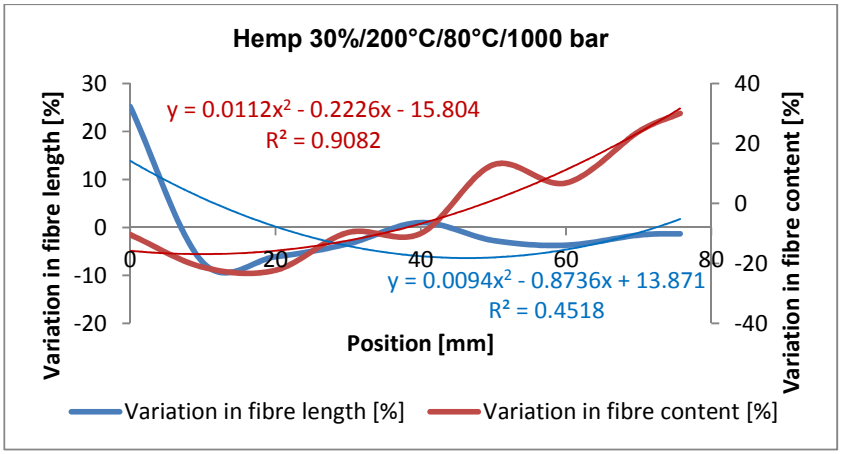
The following remarks are inferred from Figure 6-5:

- Fibre content decrease just after the injection point especially in cases of low pressure and low injection temperatures as reported also in [El-09a],
- Fibre content varies actually in a cyclic way and not simply as second degree parabolic function as seen by the trend lines shown in Figure 6-5. That is why the R^2 value is not so high. However, for the sake of comparison, the trend lines are approximated to be of the second degree function. The number of cycles increases with the increase of temperature (Figure 6-5a) or pressure (Figure 6-5b) but with smaller amplitude of variation. The fibre agglomerates are transported with the flow front leaving less fibre content at the spiral beginning (just after the injection point).
- The matching between fibre content change and fibre length change is more obvious in case of compound 3 at low temperature and pressure, see Figure 6-5e. Generally, this matching is pronounced in cellulose compounds. The regression in fibre content change of the parabolic trend lines lies within [66-93%] regardless the type of fibre, whereas the regression in case of fibre length change is high in cellulose [71-88%] and low in case of hemp [27-76%]. The reason of the relatively low regression values is simply that the trend lines are second degree polynomial function disregarding the cyclic fluctuating behaviour,

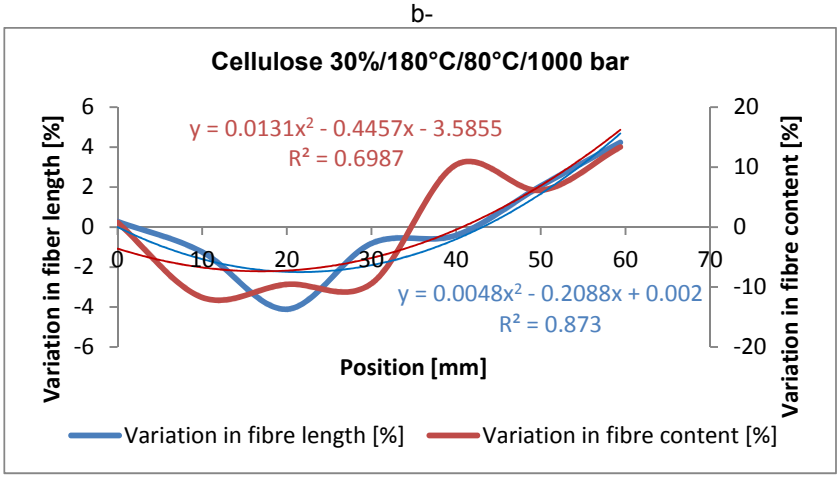
- The variation in fibre content along the spiral is clear in hemp composites more than cellulose composites (see ranges of Figure 6-5b, Figure 6-5d and Figure 6-5f).
- Effect of mould temperature is seen in Figure 6-5f. The matching between the blue and the red trend lines (fibre length and fibre content) is hardly observable by decreasing the mould temperature.



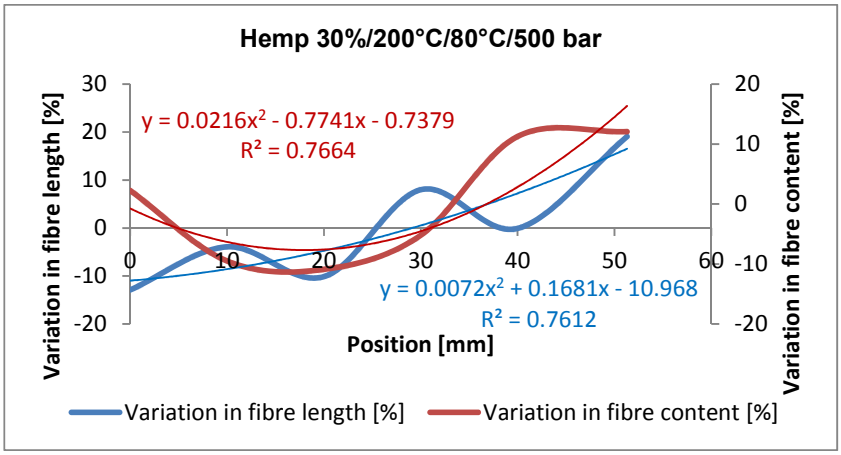
a-



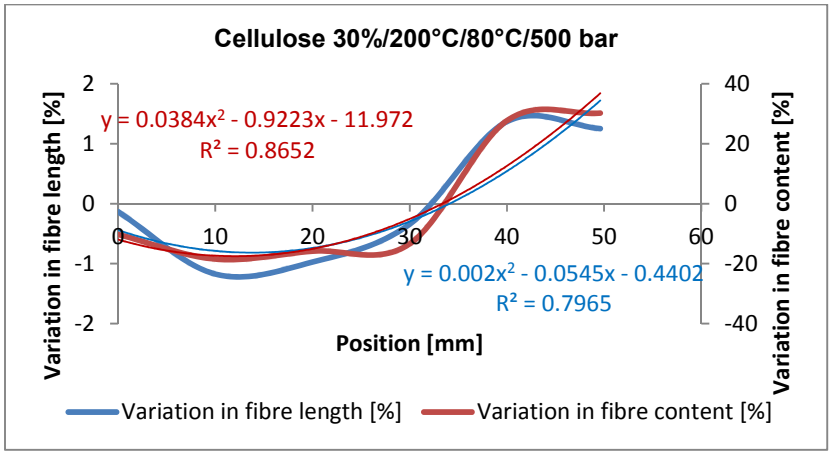
b-



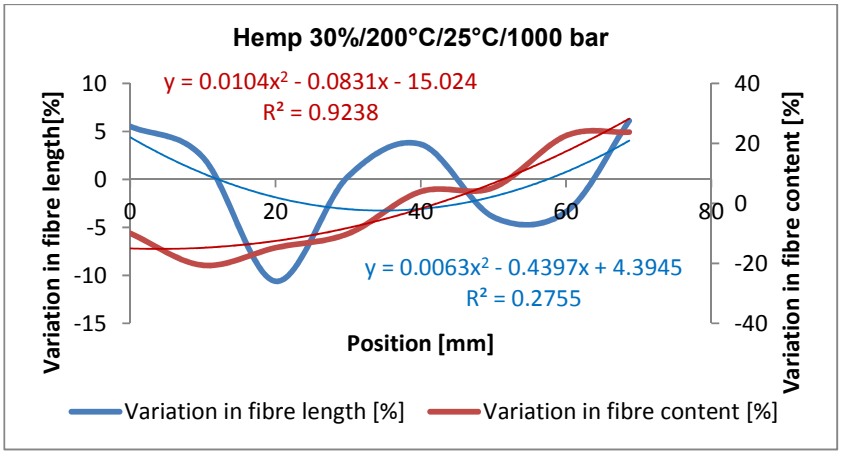
c-



d-



e-



f-

Figure 6-5: Change of fibre content along the spiral for hemp and cellulose at different mould temperatures

The blue trend lines describing the change in fibre length have low regression values especially in hemp composites. Oppositely, the red trend lines of the fibre content change have good regression and thus they can be easily described and modelled. The span of the deviation [max deviation –min deviation] is within 20-25% (6.0-7.5% deviation for 30 wt% nominal fibre content) in case of lower temperature, lower

pressure and higher mould temperature. The deviation span is studied for all the bold samples mentioned in Table 6-3, and the significance is evaluated. Pressure, temperature and mould temperature are considered continuous numeric factors while the fibre type is of category type. Figure 6-6 shows that the interaction between pressure and cellulose is significant. The interaction between temperature and cellulose comes secondly although it does not cross the significance limits. Thirdly is the interaction between the mould temperature and the polymer temperature. It is obvious also that the decrease of both the pressure to 500 bar and the temperature to 180°C decreases the deviation span whereas the decrease of the mould temperature to 25°C results in increasing the deviation span.

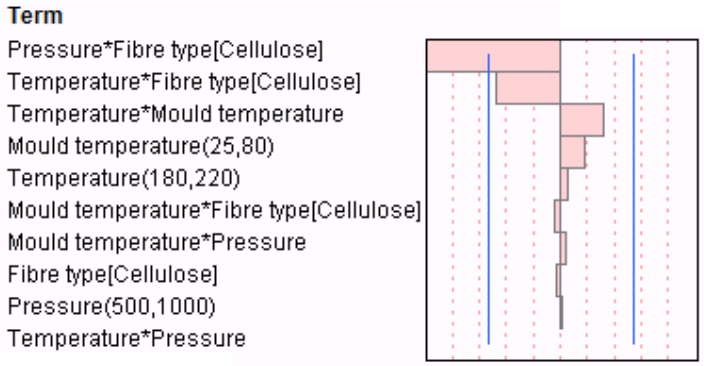


Figure 6-6: Scaled estimates of the processing parameters effect on the deviation span of fibre content using JMP

6.2.4 Outcomes

Change of fibre content and correspondingly fibre length in the injected NF/PP is proved. However it can be controlled by the processing parameters. Decreasing the pressure mainly and more or less reducing the temperature lead to smaller deviation span of fibre content change. However this pressure and temperature reductions are on the account of the high flowability and the needed low viscosity. Fibres of non-branched with high flexural strength, like cellulose, show similar behaviour of superior flowability and more homogeneity of fibre content within the injection moulded products in comparison to branched low flexural strength fibres like hemp and flax.

6.3 Modelling of flowability and fibre content distribution

6.3.1 Introduction

The phenomenon of uneven fibre content along the injection moulded polymer composites is not limited to these study findings. It is already known and reported for long time [Fér09], [Sch05], [Ram14], [Kub74]. The modelling of the fibre distribution is necessary to expect the final part overall mechanical properties as well as its physical behaviour during solidification, shrinkage and hence its warping. However, there is up

till now no solid commercial software package that can predict fibre content distributions in a moulded part [Lon11]. Londono-Hurtado et al. [Lon11] tried to construct an algorithm for predicting the fibre separation under different moulding parameters such as viscosity, fibre size and fibre nominal content. Fibres are modelled as chains of connected rigid beads with controllable flexibility. Then a mechanistic simulation of fibres to predict their position is developed as in Equation 6-3.

$$\frac{dX_v}{dt} = u_v + \frac{1}{\zeta}(f_v^{xv} + f_v^c + f_v^b + f_{v\mu}^f + f_v^l)$$

Equation 6-3

Where U_v is the unknown velocity of the bead at position X, ζ is the bead friction coefficient, the right hand coefficients within brackets are the excluded volume forces acting on the bead, the connector force between neighbouring beads, the fibre bending force, the friction force between beads v and μ and the lubrication force respectively. These forces are in balance with the hydrodynamic drag force according to the free body analysis. The change in position X can be estimated by solving the normal mass continuity equation. Then the unknown bead (fibre) speed is calculated position and hence the position can be found by integration.

Londono-Hurtado et al. [Lon11] reported that the change in fibre content is proportional parabolically with fibre aspect ratio due to the fibre entanglement and hence its slower movement. Also he reported that fibre content decreases at the fluid front due to fibre separation but this is in opposite to the experimental findings of [Kub74] and [Ram14]. Anyway this proposed algorithm [Lon11] has an advantage that it can deal with flexible fibre like natural fibres and not like the Folgar-Tucker method that deals with the short fibres with minimum fibre flexibility as described in Equation 6-4. CI is the interaction coefficient, ψ is the fibre distribution function, t is the time and ϕ is the fibre angle. This equation is solved after assuming the fibre distribution at t=0.

$$\frac{d\dot{\gamma}}{dt} = C_{I\dot{\gamma}}\frac{\partial^2\psi}{\partial\phi^2} - \frac{\partial}{\partial\phi}\left(\psi\left(\sin\phi\cos\phi\left(\frac{\partial v_y}{dy} - \frac{\partial v_x}{dx}\right) - \sin^2\phi\frac{\partial v_x}{dy} + \cos^2\phi\frac{\partial v_y}{dx}\right)\right)$$

Equation 6-4

6.3.2 Empirical description of flowability and fibre content distribution

To study the flowability quantitatively, flowability study, as explained in 6.2, is carried out for composites with either cellulose or hemp. The factors considered are the injection pressure, temperature and mould temperature. For cellulose, an additional factor is also studied namely the fibre content (10, 30%). Fitting equations are calculated using the JMP (least square analysis) and found to be as follows in Equation 6-5 and Equation 6-6:

$$FL_{Cellulose} = 84.4 - 26.4\left(\frac{FC-20}{10}\right) + 17.5\left(\frac{P-750}{250}\right) + 7.9\left(\frac{T-200}{20}\right) - 5.2\left(\frac{P-750}{250}\right).\left(\frac{FC-20}{10}\right) + 2.0\left(\frac{P-750}{250}\right).\left(\frac{T-200}{20}\right) + 1.4\left(\frac{Tm-52,5}{27,5}\right) - 2.8\left(\frac{T-200}{20}\right).\left(\frac{T-200}{20}\right) + 0.9\left(\frac{T-200}{20}\right).\left(\frac{Tm-52,5}{27,5}\right) - 0.4\left(\frac{P-750}{250}\right).\left(\frac{Tm-52,5}{27,5}\right)$$

Equation 6-5

$$FL_{Hemp} = 60.7 + 11.5\left(\frac{P-750}{250}\right) + 9.0\left(\frac{T-200}{20}\right) + 1.14\left(\frac{P-750}{250}\right).\left(\frac{T-200}{20}\right) + 3.0\left(\frac{Tm-252,5}{27,5}\right) - 0.8.\left(\frac{T-200}{20}\right)..\left(\frac{T-200}{20}\right) + 0.9.\left(\frac{T-200}{20}\right).\left(\frac{Tm-252,5}{27,5}\right)$$

Equation 6-6

Where (*FL)* is the flow length in cm, (*P)* is the pressure in bar, (*FC)* is the fibre content in %, (*T)* is the temperature of the injected polymer in °C and (T_m) is the mould temperature in °C.

Similarly, the deviation in fibre content is defined as a function of the following parameters (Polymer injection temperature, mould temperature, injection pressure, and finally the normalised distance covered '*X/L*'). 'X' is the distance between the injection point and the point under investigation.

'L' is the equivalent spiral flow length at certain P, T and Tm according to the type of fibre in Equation 6-5 and Equation 6-6. So 'X/L' lies between 0 and 1 values.

This function does not include the original fibre content (10 or 30 wt%) into consideration to reduce the burden of the required fitting terms.

The predicted expressions according to the statistical analysis of JMP software are presented in Equation 6-7 and Equation 6-8.

$$FC\_Change\%_{Cellulose} = -3,462 - 2.335\left(\frac{T-200}{20}\right) - 2,415\left(\frac{T-200}{20}\right)\left(\frac{T-200}{20}\right) - 0,059\left(\frac{Tm-52,5}{27,5}\right) + 0,166\left(\frac{P-750}{250}\right) + 11,74\left(\frac{X/L-0,5}{0,5}\right) + 0,178.\left(\frac{T-200}{20}\right)\left(\frac{X/L-0,5}{0,5}\right) + 3,187\left(\frac{X/L-0,5}{0,5}\right)\left(\frac{Tm-52,5}{27,5}\right) - 9,406\left(\frac{P-750}{250}\right).\left(\frac{X/L-0,5}{0,5}\right) + 7,584\left(\frac{X/L-0,5}{0,5}\right)\left(\frac{X/L-0,5}{0,5}\right)$$

Equation 6-7

$$FC\_Change\%_{Hemp} = -4{,}023 - 0.378\left(\frac{T-200}{20}\right) - 0{,}4\left(\frac{Tm-52{,}5}{27{,}5}\right). + 0{,}125\left(\frac{P-750}{250}\right) + 13{,}908\left(\frac{X/L-0{,}5}{0{,}5}\right)$$
$$+ 17{,}278\left(\frac{T-200}{20}\right).\left(\frac{X/L-0{,}5}{0{,}5}\right) + 1{,}203.\left(\frac{X/L-0{,}5}{0{,}5}\right).\left(\frac{Tm-52{,}5}{27{,}5}\right). + 8{,}967\left(\frac{P-750}{250}\right).\left(\frac{X/L-0{,}5}{0{,}5}\right) +$$
$$7{,}32\left(\frac{X/L-0{,}5}{0{,}5}\right).\left(\frac{X/L-0{,}5}{0{,}5}\right).$$

Equation 6-8

A comparison between the empirical equations (predicted model) and the experimental results are presented in Figure 6-7. The ‘P-value’ is a figure for the statistical significance for matching between the experimental and model results. ‘P-value’, as shown in Figure 6-7, is less than 0.0001 (extreme significant. This is also ensured by the R-squared (r²) and RMSE results. r² is a relative measure of fit. It is the fraction of the total sum of squares that is 'explained by' the regression. Its value lies between 0 and 1.

$$r^2 = 1 - \frac{\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2}{\sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2}$$

Equation 6-9

Where ‘Yi’ is the the value at the ‘i’ observation. ‘n’ is the number of observations. $\hat{y}$

Is the estimated value for this observation number ‘i’ and $\bar{y}$ is the average value for all observations. RMSE is the root mean square of the summation of the squared errors as in Equation 6-10.

$$RMSE = \sqrt{\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2}$$

Equation 6-10

RMSE has the useful property of being in the same units as the response variable. RMSE of PP/Cellulose is less than that of PP/Hemp as expected indicating higher regression of the experimental results with respect to the model ones.

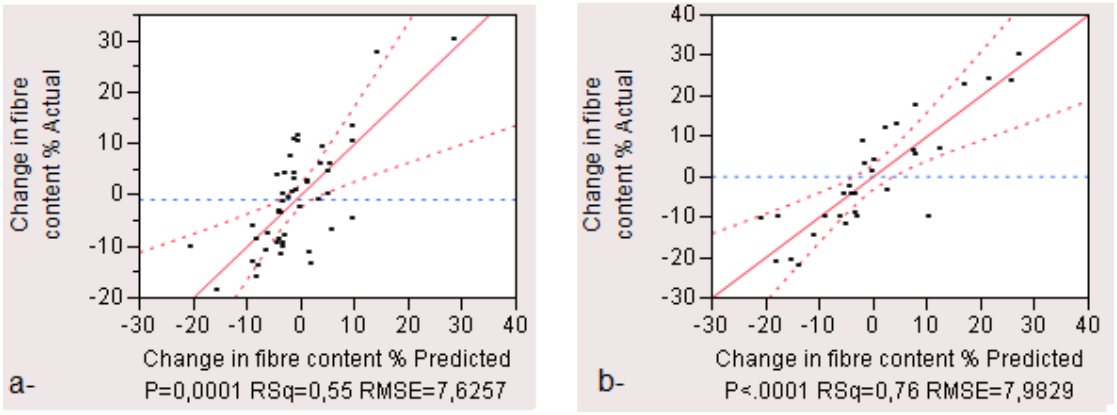


Figure 6-7: Comparison between the experimental (actual) and model (predicted) results out of Equation 6-7and Equation 6-8 for a- Cellulose b- Hemp

The sorted parameter estimates of both statistical studies are shown in Figure 6-8. It is obvious that the most significant parameters that influencing the fibre content distribution are: the normalised distance 'X/L' alone or its self-interaction or with temperature, mould temperature and pressure.

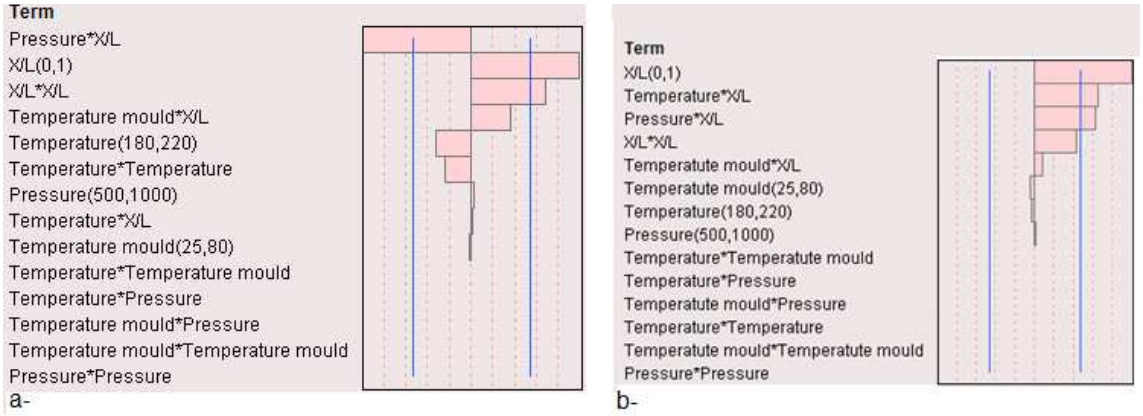


Figure 6-8: Comparison between the sorted parameter estimates for a- Cellulose b- Hemp

6.3.3 Case study: The fibre content in injected plates (Experimental vs. Model)

The validity of the empirical equations, extracted from one-dimension spiral as mentioned previously, will be examined in a two-dimensional plate with a relative large area. The plate dimensions are 298x158x3 mm^3, Figure 6-10a , and the injection point is located at the middle of the 158 breadth edge. The material is PP with 30% cellulose fibres. Injection pressure is 900 bar and temperature is 210°C. Mould average temperature is 52°C.

The following assumptions are taken into consideration in this modelling of this case study:

- The plate thickness is assumed similar to that of the spiral effective thickness. Therefore, the flow length (*FL*) for each point in the plate is calculated according to Equation 6-5 and Equation 6-6 for cellulose and hemp respectively.
- Hemp and flax are assumed to have similar equations because both are bast fibres.
- It is assumed for the sake of simplicity that the flow of NFTC melt is a one-way trajectory and the fluid stops moving just after completing the mould filling.
- The 'X' distance is calculated with respect to the injection point as shown in Figure 6-10a. 'L' is calculated from Equation 6-5. Hence the (X/L) value is calculated and the fibre content is calculated according to Equation 6-7.

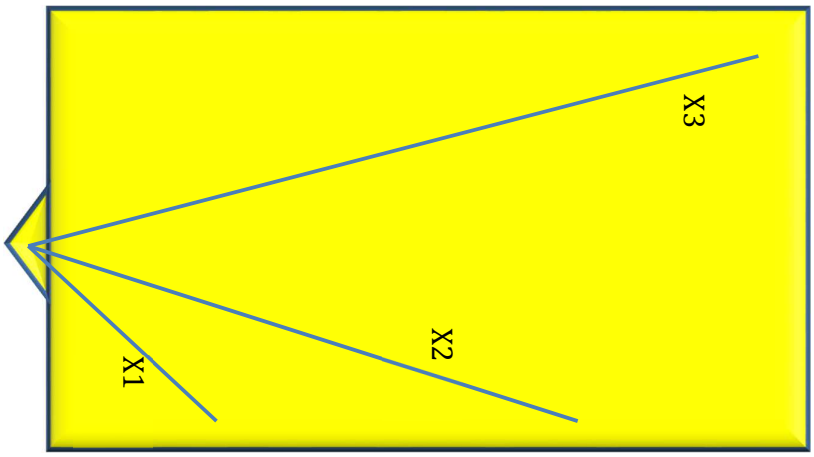


Figure 6-9: The injected plate and the Positions of points under investigation

Accordingly the fibre content distribution is plotted in Figure 6-10. Fibre content decreases slightly to 27.1% after the injection point then increases again till 32.5%. Three samples are cut along the middle longitudinal axis of the sample at the beginning, the middle and the end. The (experimental/ model) results are (28.5 /28.3, 29.4/28.8, 32.4/32.7%) for the three points respectively.

Repeating the same procedure with PP/30% Flax shows wider distribution of fibre content with a range of 23-36%, as in Figure 6-11. Comparing the model results against the experimental extracted fibres at the same three points along the middle longitudinal axis, the results are found to be (27.9/23.0 , 29.2/29.2 , 33.8/35.6) respectively. The matching is remarkable at the second and the third point whereas 4% difference is found at the first point due to the problematic nature of the flexible fibre.

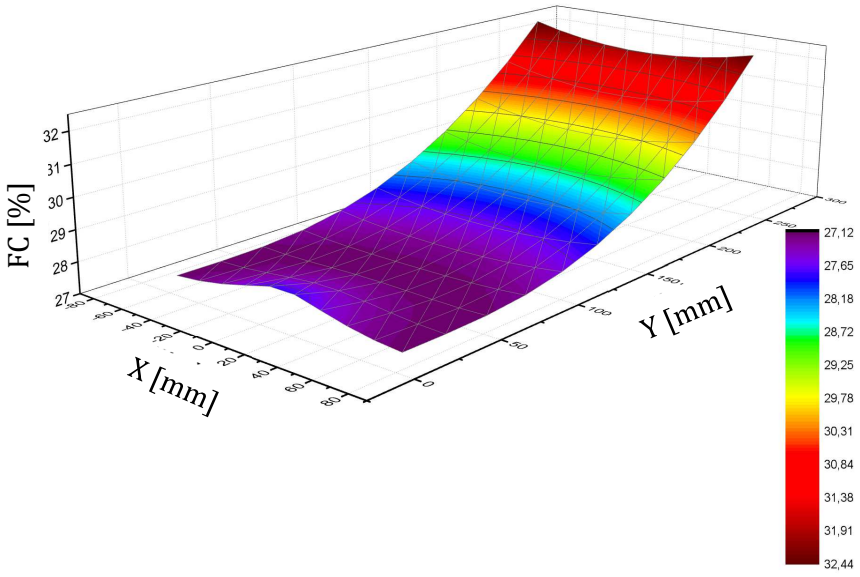


Figure 6-10 Fibre content along the injected plate of PP/30% Cellulose

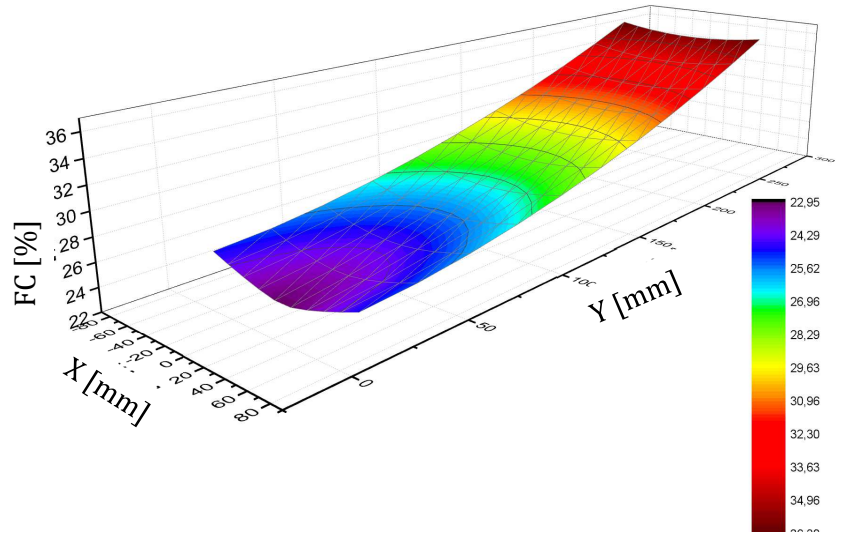


Figure 6-11: Fibre content along the injected plate of PP/30% Flax

6.3.4 Final comment about the fibre distribution in NFTC products

The empirical equations developed in 6.3.2 gives a matching feasible solution for the fibre content distribution in the injected samples. However this problem should be in future work treated analytically. Actually, the phenomenon of different fibre contents along the injection moulded samples is a typical multiphase flow where PP and fibres are single phase regions.

Most of the available recent work in this direction is limited to fibre orientation and length and not to fibre content distribution [Lon11] [Ngu11] in spite of its effect on the

mechanical properties and the geometry accuracy. Even the new software modules like 3d Timon supplied by ESI group [Nak14] tried to overcome the limitations of the Folger-Tucker formulation [Ngu11] and use the mechanistic model [Lon11]. However, it still misses the handling of the problems facing NFTC like (fibrillation or fibre thermal decomposition and complicated fibre shapes) and their final effect on the mechanical properties.

7 Additives for improving properties of NFTC

7.1 Improving the impact strength of NFTC

7.1.1 Introduction

The attractive properties of NFTC, in comparison with glass fibre composites, are close specific strength, light weight and lower mould abrasion for injection moulding processes besides a better environmental impact [Ble02], [Tor07], [Yu08]. However, there are other negative factors, such as incompatibility between the polar fibre and the non-polar thermoplastic matrix [Lee08], water absorption and hence dimension instability [Tah06], rotten smell accompanying the bacterial degradation [Bos04], inconsistency of the mechanical properties due to the variations in the natural fibre sources or harvesting time [Ble02] and the limited range of compounding temperatures [Ble02] [Mor07]. A very important drawback of NFTC is the low toughness and the corresponding reduced impact strength which arouse the need for investigating different ways for impact strength improvement.

Ruksakulpiwat et al. [Ruk09] uses both the natural and synthetic rubber (ethylene propylene diene monomer EPDM) as elastomeric substances to improve the polypropylene PP composite filled with 20 wt% vetiver grass. In this study [Ruk09], different portions of the rubber in the range of 0-50% are added with respect to the composite. The impact strength and the elongation of the composite are enhanced for rubber content more than 10%. On the other hand, the strength and the young's modulus fall tremendously below the pure PP values. Up to 10% rubber, the mechanical strength and tensile modulus are kept with insignificant improvement in impact strength and elongation. More than 10% rubber results in increased impact and elongation. Meanwhile the E-modulus and tensile strength are decreased. This is attributed to the higher viscosity of rubber and hence lower crystallinity. Natural rubber has slightly lower viscosity in comparison with EPDM. Thus EPDM treated NFTC has relatively higher tensile and impact strengths.

The same way of impact strength improvement is followed by Manchado et al. [Lóp03]. 20 and 30 wt% of EPDM are added to PP 20% flax composite and mixed by hot roll kneading. Both PP and EPDM are investigated with and without maleic anhydride functionalisation. Quick crystallisation and better adhesion are observed due to the presence of maleic anhydride. Significant improvement and elongation are attained with EPDM. However, the tensile strength deteriorates in comparison to the non-treated composite. It is claimed that EPDM also enhances the nucleation and crystallisation process.

Oksman et al. [Oks03] attempted to improve the bio-composite impact strength of Polylactic acid PLA filled with 40 wt% flax using the triacetin. Triacetin enhanced the PLA impact strength with 20-26% when treated with triacetin at 5-15 wt%. Compounding is carried out by a twin screw extruder. No improvement in impact strength was recorded; in the opposite a 1-3% decrease was measured. Oksman et al [Oks03] concluded that the addition of triacetin plasticiser is not positive regarding the

composite impact strength properties. This result of Oksman [Oks03] is attributed to the change in the fibre structure to a brittle nature as a result of the triacetin. However, this conclusion of Oksman et al [Oks03] may not apply when no coupling agents, that bind the polymer with the fibres, are used. The deterioration in mechanical properties indicated by Oksman [Oks03] could be interpreted in terms of the lack of a coupling agent especially with such huge reported flax percentage , 40 wt%.

Glycerol is used as a plasticiser with natural fibre [Sai08] and wood fibre [Taj08] composites. As reported in [Sai08], only 3% glycerol is added to the blend of wood PP composite. But in case of natural fibres, glycerol is added in an equivalent quantity to the natural fibre [Sai08]. Glycerol shows better results regarding the values of impact [Sai08] and elongation [Taj08].

Away from the previous three chemical ways, the addition of another type of natural fibre can induce an improvement in the impact strength for two reasons; either the fibril angle [Mie00], [Gra09] or the cellulose content. Cellulose is the main load bearing element in the composite system besides to the quality of the interfacial adhesion. Reich-Albrecht [Rei10] uses the natural nettle fibres which is characterised with its high cellulosic content. Graupner [Gra09] attempted to combine the effect of high fibril angles like cotton and man-made lyocell cellulosic fibres with the low fibril angle like bast fibres. As a result, composites of better impact strength and strength are achieved.

This study focuses on the comparison between the methods used to improve the impact strength property of the natural fibre composites. Hybrid natural fibres of flax/ nettle are used as a first method. Elastomer addition is also tried and finally triacetin as plasticiser. Triacetine is selected instead of glycerol because of the availability of literature data about its effect with natural fibre PP composites [Taj08].

7.1.2 Systematic plan of work

Two composites of polypropylene filled with 30 and 50 weight % of flax are taken as case studies. First method implies the hybridisation of the flax with nettle fibres which are characterised by their higher cellulosic contents. Second method represents the addition of an elastomer which is ethylene propylene diene monomer EPDM with 5 and 10 weight %. Finally, triacetine as a plasticizer agent is tried with different percentages of 5, 10, 15 and 20 weight %. Table 7-1, Table 7-2 and Table 7-3 illustrate the factors investigated in this study. Some samples such as A7, A8, B11, B12 contain no flax in order to designate the effect of EPDM and triacetin on the PP matrix for comparison purposes. Samples A1, B1 and C1 are the same representing the reference composite of 30 wt% flax. Samples A4, B6 and C8 are also similar to represent the samples of 50 wt% flax.

The selected fibres in this study are flax and nettle fibres, Table 3-1. Nettle contains 92% cellulose which is more than 82.5% for the flax [Rei10]. Pre-treatment with alkalinisation is essential. 2% NaOH solution is used to alkalinise the flax and nettle fibres for 24 hours. Fibres are then washed with distilled water till neutralisation

(checked with PH meter). Fibres are then dried for 48 hours at 100°C. Before compounding the flax fibres with the PP matrix, the fibres are re-dried again for an hour minimum.

Homopolymer PP, as mentioned in 3.2.2, is used as the host thermoplast. Two levels of fibre contents are selected for this plan due to their wide usage namely 30 and 50%. Granulated form MAPP, as mentioned in 3.2.3, is used to couple PP with the natural fibre through its hydroxyl group.

The used impact modifiers, according to Table 3-3, are triacetin (Plasticizer, an ester compound of glycerin and acetic acid, Figure 7-1) and EPDM (elastomer).

Table 7-1. Experiments using EPDM

Sample #	PP	MAPP	Flax	Synthetic elastomer EPDM
A1	67	3	30	0
A2	62	3	30	5
A3	57	3	30	10
A4	45	5	50	0
A5	40	5	50	5
A6	35	5	50	10
A7	95	0	0	5
A8	90	0	0	10

Table 7-2. Experiments using triacetin

Sample #	PP	MAPP	Flax	renewable plasticizer Triacetin
B1	67	3	30	0
B2	62	3	30	5
B3	57	3	30	10
B4	52	3	30	15
B5	47	3	30	20
B6	45	5	50	0
B7	40	5	50	5
B8	35	5	50	10
B9	30	5	50	15
B10	25	5	50	20
B11	80	0	0	20
B12	90	0	0	10

Table 7-3. Experiments using hybrid fibres (nettle addition to the flax)

Sample #	PP	MAPP	Flax	Nettle fibre
C1	67	3	30	0
C2	67	3	25	5
C3	67	3	20	10
C4	67	3	15	15
C5	67	3	10	20
C6	67	3	5	25
C7	67	3	0	30
C8	45	5	50	0
C9	45	5	40	10
C10	45	5	30	20
C11	45	5	20	30
C12	45	5	10	40
C13	45	5	0	50

Compounding mechanism is carried out in a kneader at 180°C, 50 rpm and 20 minutes. PP is added at first followed by MAPP. Finally, natural fibres are added gradually within 5-6 minutes. In the case of samples containing EPDM, EPDM is added after the compounding of PP and MAPP, whereas in case of triacetin, the flax fibres are immersed in triacetin for 2 hours before the insertion of fibres into the kneader. The remaining triacetin liquid drops are poured into the composite blend during compounding. Compounded material is then shredded. Granules are injection moulded to mechanical samples at a temperature pattern of 185-190-195-200°C using Allrounder 220C 600-250, Arburg, Lossburg, Germany.

Samples of mechanical testing are conditioned at 23°C/50% relative humidity for at least 88 hours according to ISO 291 for test room conditions. Test sample is injection moulded to the 1BB form (Width*thickness*gauge length = 2*2*10 mm3) according to ISO 527-2. Test is conducted and evaluated according to ISO 527-1. Tensile strain rate is 2 mm/min for 10 specimens. Modulus of elasticity is calculated as the slope of the stress-strain curve at the recommended strains (0.0005 and 0.0025) in ISO 527-1. Un-notched Charpy samples are injection moulded and adapted also according to ISO 291. Sample cross section is 2*4mm². 10-15 samples are tested according to ISO 179-1 with 1 j striker.

Water absorption test is conducted also according to DIN 53495-method 3 where the weight of the sample is observed after 30 min in 100°C hot distilled water followed by 15 min in 23°C distilled water and finally drying of the sample.

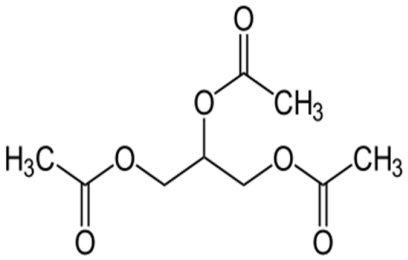


Figure 7-1: Triacetin chemical structure

7.1.3 Results of the impact modifiers addition

The effect of the impact modifiers is to be discussed in the following section. The results will be listed firstly into three groups (A: EPDM as an elastomer, B: Triacetin as a plasticiser, C: Hybrid fibres by adding nettle to flax). The results of each of these three groups are classified to the two natural fibre contents in the NFTC (30 and 50 wt%).

A- EPDM group

Figure 7-2 shows that the addition of EPDM has a slight negative effect especially for the E-modulus. E-modulus is sensitive for EPDM at 5% while tensile strength starts to decrease apparently at EPDM in the range of 5-10%. Figure 7-3 shows that the addition of EPDM has a negative effect on the impact strength but on the other side the elastomer presence helps in increasing the elongation.

Figure 7-4 is similar to Figure 7-2 where the same negative effect is observed with composites filled with 50% flax. Both E-modulus and strength shows obvious negative trends. Figure 7-3 shows that EPDM improves both the impact strength (8-9%) and elongation. In other words, EPDM shows its required effect only when used with excessive amount of flax (50%). Although the standard deviations of impact strength in Figure 7-5 are large, the relations, obtained for impact strength and elongation, are statistically significant using the simple statistical t-test with a significance of more than 95%.

These results match with Manchado et al. [Lóp03]. EPDM hinders the trans-crystallisation and hence low interfacial shear strength is attained from the single fibre pull-out test. The explanation of this behaviour is attributed to EPDM elastomer particles which act in the PP matrix as stress concentration points [Lóp03]. Thus local yielding takes place throughout the sample tensioned cross section and hence avoiding sudden failure.

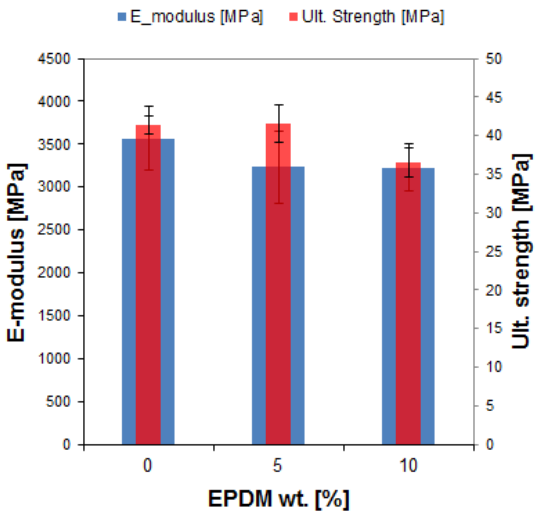


Figure 7-2: E-modulus and ultimate tensile strength of PP/30 wt% flax with different EPDM contents

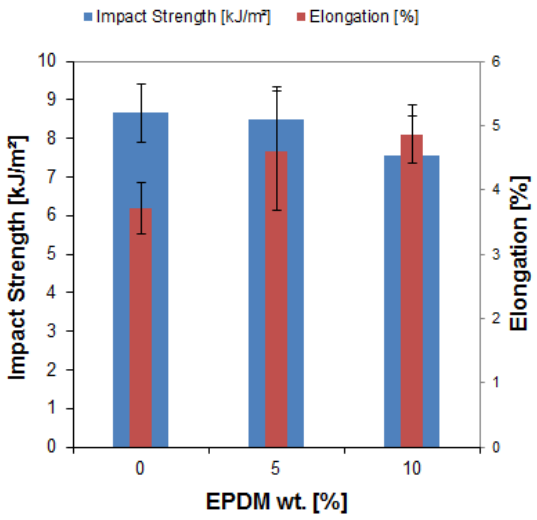


Figure 7-3:: Impact strength and elongation of PP/30 wt% flax with different EPDM contents

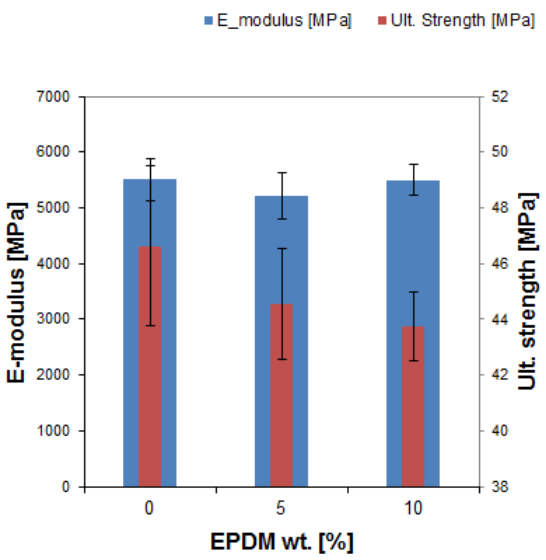


Figure 7-4: E-modulus and ultimate tensile strength of PP/50 wt% flax with different EPDM contents

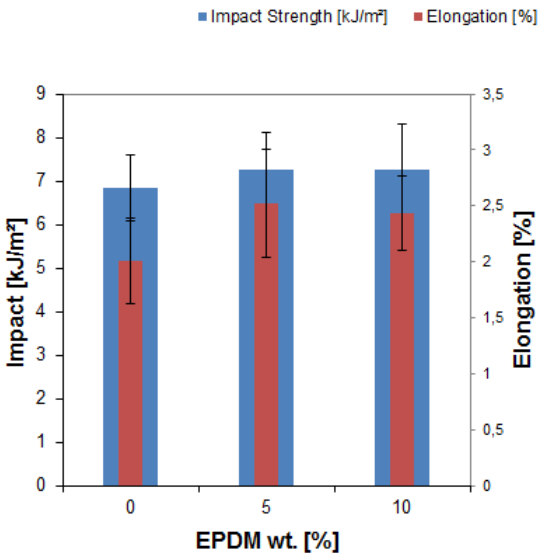


Figure 7-5: Impact strength and elongation of PP/50 wt% flax with different EPDM contents

B- Triacetin group:

Compared with EPDM, triacetin has obviously negative effect on both E-modulus and strength as shown in Figure 7-6. Figure 7-7 shows however a stable impact strength and a slight improvement in elongation at 15 and 20% triacetin.

Once more, Figure 7-8 shows the same negative effect of triacetin on the strength and E-modulus for composites filled with 50% flax. This negative result of triacetin addition

matches with [Wal04] where triacetin, up to 5%, has improved the impact strength of PLA. On the other hand, the impact strength decreases when short chopped flax fibres are added. Oksman et al. [Oks03] reported as well that the addition of triacetin did not promote any improvement in composite properties. Figure 7-9 shows a negative trend for impact strength and insignificant stable elongation. In this part of the study, the addition of MAPP is assumed to have the plasticisation effect of triacetin as well as the improved interfacial strength by MAPP. However, the worse result disaproves with the assumption. Therfore, triacetin effect on the the impact strength is inferior to that of EPDM as shown in Figure 7-5.

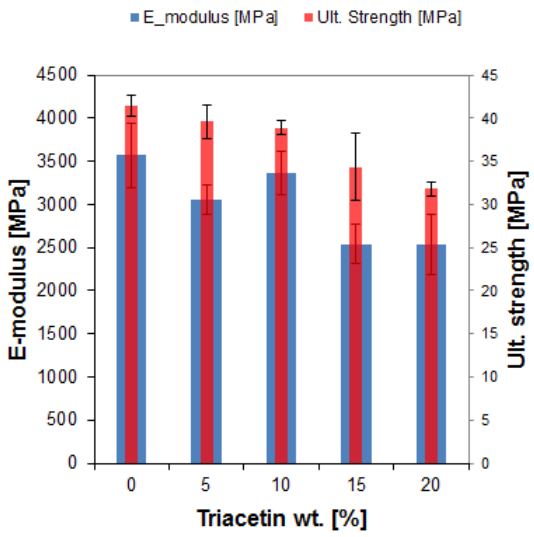


Figure 7-6:: E-modulus and ultimate tensile strength of PP/30 wt% flax with different Triacetin contents

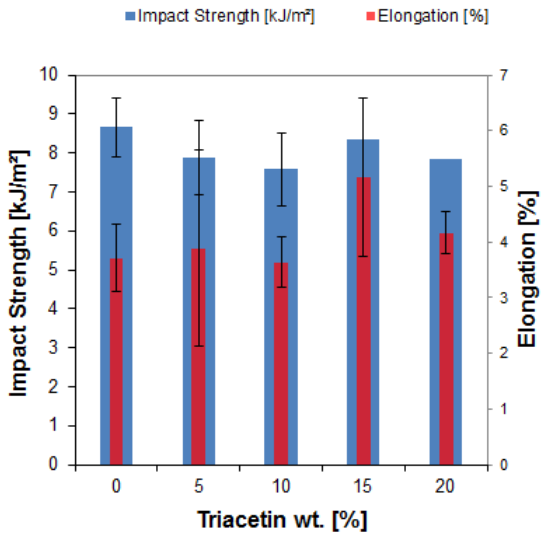


Figure 7-7:: Impact strength and elongation of PP/30 wt% flax with different Triacetin contents

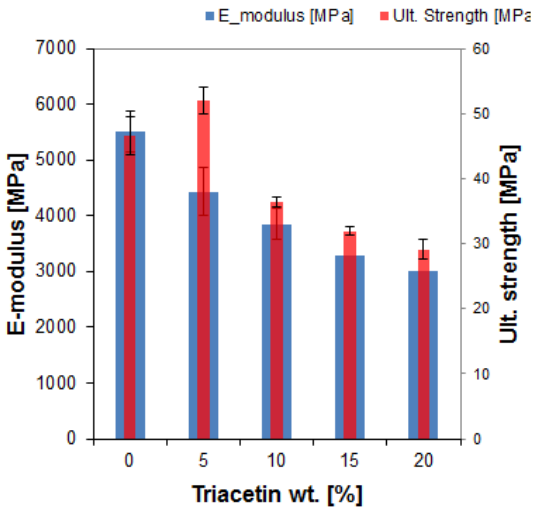


Figure 7-8: E-modulus and ultimate tensile strength of PP/50 wt% flax with different triacetin contents

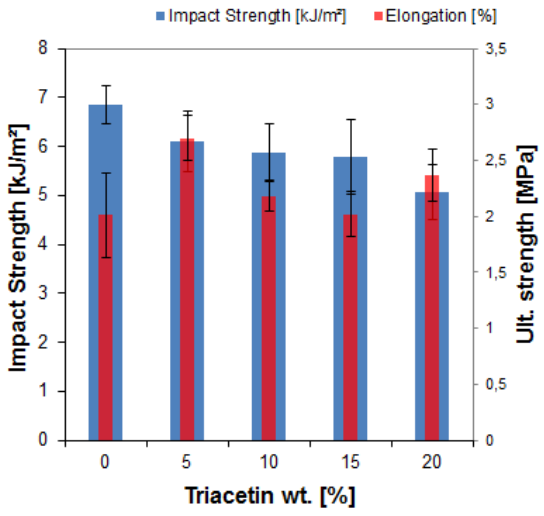


Figure 7-9: Impact strength and elongation of PP/50 wt% flax with different Triacetin contents

C- Nettle fibres group:

Figure 7-10 shows that replacing flax fibres with nettle fibres does not have any significance in strength and E-modulus. Figure 7-11 shows that replacing flax fibres with nettle fibres improves the elongation and impact strength (20%).

For the composite filled with 50% fibre, Figure 7-12 is similar to Figure 7-10 where trivial change in strength or E-modulus is noticed in account of replacing flax with nettle. Similar to Figure 7-11, Figure 7-13 shows that the replacement of flax with nettle presented a positive effect on impact strength (35%) and elongation. The addition of 10-15 wt% of nettle fibres instead of flax improves the impact strength with 11-16 wt%. This is explained in terms of the fibre twist angle as defined in section 2.1.1. The nettle fibre angle (almost 3°) is less than the flax fibril angle (10-11°) [Mue12]. Therefore, higher tensile strength value of the nettle polymer composite than flax could be easily explained. Moreover and in addition to the lower nettle twist angle, there are other two reasons which explain the better mechanical properties attained by nettle:

- The higher cellulosic content in nettle,
- The smaller fibre diameter of nettle allows getting to higher aspect ratio even after the damaging kneading process. Additionally, the small diameter allows easier sliding of fibres in case of mechanically stressing the composite sample.

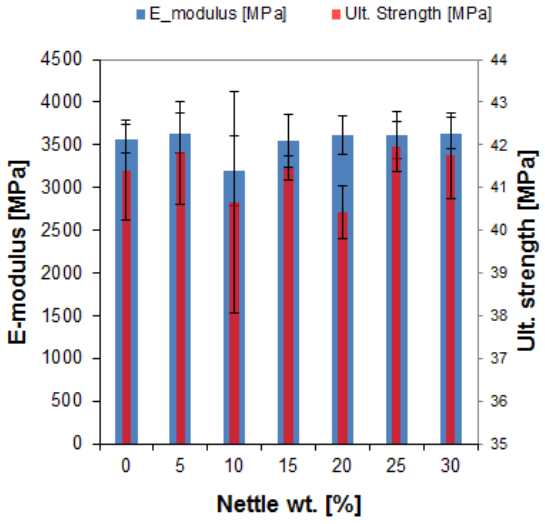


Figure 7-10: E-modulus and ultimate tensile strength of PP/30 wt% fibre with different nettle contents

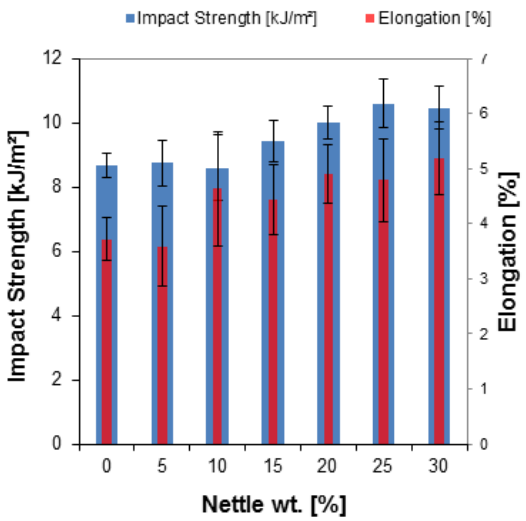


Figure 7-11: Impact strength and elongation of PP/30 wt% fibre with different nettle fibre contents

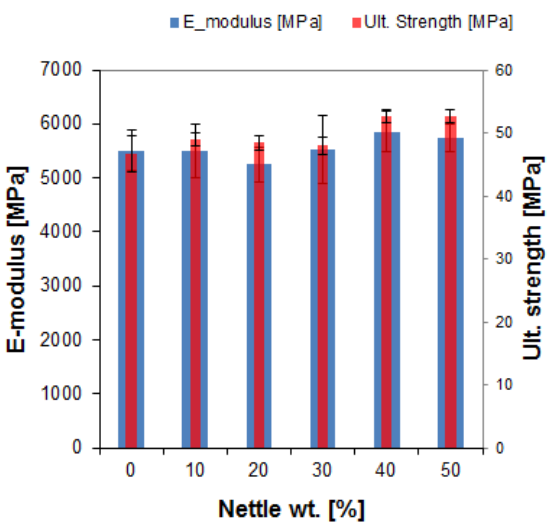


Figure 7-12: E-modulus and ultimate tensile strength of PP/50 wt% fibre with different nettle contents

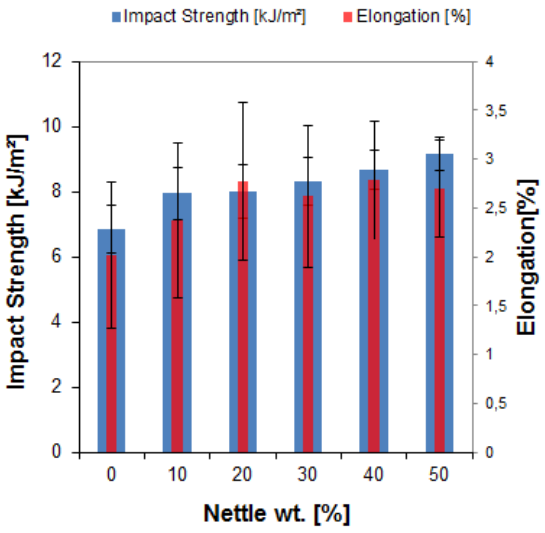


Figure 7-13: Impact strength and elongation of PP/50 wt% fibre with different nettle fibre contents

Figure 7-14 summarises the effect of EPDM, triacetin and nettle on the composite impact strength. Only triacetin represents negative effect regardless the fibre content. EPDM shows a negative influence only for composites containing 30% flax. Nettle shows a comparatively positive influence in impact strength.

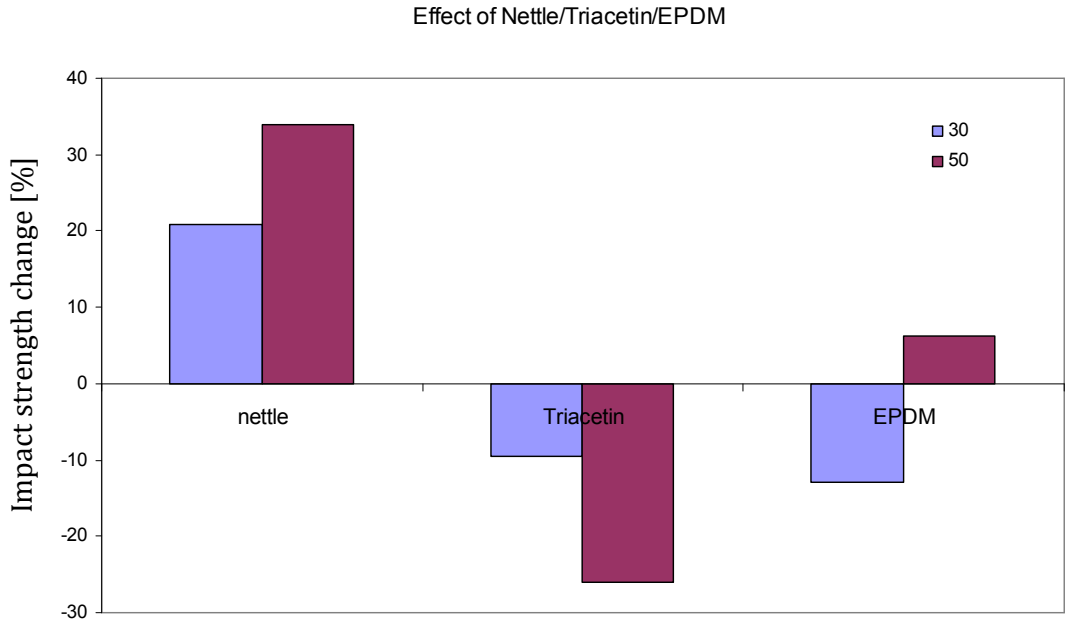


Figure 7-14: Change in impact strength due to Nettle, Triacetin and EPDM for both the 30 and 50 wt% flax groups

The fracture of the tensile samples also points out to the effect of triacetin and EPDM. Samples filled with 30% (nettle and flax) show abrupt failure. Whereas the plasticiser triacetin and the elastomer EPDM, at 30% flax, show that the tensile test terminates after soft breaking. The two halves of the sample are still in contact after the test and did not separate like the flax/nettle composite samples. This behaviour of soft failure is illustrated in Figure 7-15a. Figure 7-15b presents the corresponding tensile behaviour to show the span of elongation after reaching the maximum strength. Abrupt fracture is noticed by the short span in case of using fibres without impact modifier and longer span for triacetin and EPDM samples. Figure 7-15c shows the effect of the triacetin content on the tensile and fracture behaviour of the samples. The sketch shows the elongated samples with the addition of triacetin, where the straight failure denotes sudden break-up. When the triacetin is added, the sample elongates and performs slight necking and straight failure vanishes. This is attributed to the distribution of stress within a bigger deformation area. Hence gradual and not abrupt fracture dominates the failure behaviour.

The semi-crystalline samples are characterized with larger tendency towards off-branching or bifurcation [Gal03] more than to induce crazing as in the amorphous polymers. Branching implies the need for more energy to continue fracture as shown in Figure 7-16. The distance-before-branching (X) will be taken as an indicator for the branching start. Shorter distance points to more branching and thus renders higher impact strength. Increase of nettle percent leads to shorter length before branching (more ductility) as shown in Figure 7-17c with respect to the longer length in Figure 7-17a and Figure 7-17b.

Higher impact strength is also observed in 10 % EPDM with 30% flax, Figure 7-17d. This can be explained by the shape of the fracture line where the fracture line is making a zigzag pointing to branching occurrence and hence higher impact strength. The sample of 15% Triacetin in Figure 7-17e has not shown significant increase in the distance-before-branching but the zigzag behaviour is still present pointing to branching likelihood.

In Figure 7-18 composites filled with 50% fibre (flax+ nettle) show increased water absorption. This is attributed to the hydrophilic nature of the fibres in contrary to the hydrophobic nature of PP. This result matches the findings of Wang et al. [Wan06]. Figure 7-18 shows also a logarithmic decrease in water absorption for the composites when nettle fibres are added instead of flax. For instance, water absorption decreases from 0.96% (only flax) to 0.58% (only nettle) in case of composites filled with 50% fibres. Meanwhile, the composites filled with 30% fibres show that water absorption decreases from 0.8% (only flax) to 0.42% (only nettle). Here shines the argument why nettle shows such enhancement to composites in resistance to water absorption. This can be explained by the Fick's law of diffusion as shown in Equation 7-1 [Ric99], [Wan06].

Assuming the similar diffusion coefficient (around 30E13 cm²/s at 70°C and 30% fibre [Esp04]), Equation 7-1 is simplified to Equation 7-2. The same water exposure time

(30 min) according to DIN 53495 is used in the water absorption test. The average fibre diameters of flax and nettle are 39 μm and 69 μm respectively [Mue10a].

Then the reciprocal ratio of the fibre diameter is (69/39)=1.8 and the ratios of water absorption for flax: nettle for the 30 and 50% composites are (0.96/0.58=1.7) and (0.8/0.42=1.9) respectively. The results are matching with the diffusion equation.

$$M_t = \frac{2M_\infty}{l}\sqrt{\frac{Dt}{\pi}}$$

Equation 7-1

$$M_t \alpha \frac{1}{d}$$

Equation 7-2

Where 'M_t' denotes the amount of diffusion at time 't,', 'M_∞' denotes the diffusion at infinite time. 'd' is the diffusion coefficient. 'l' denotes the sample thickness or the fibre diameter after simplification.

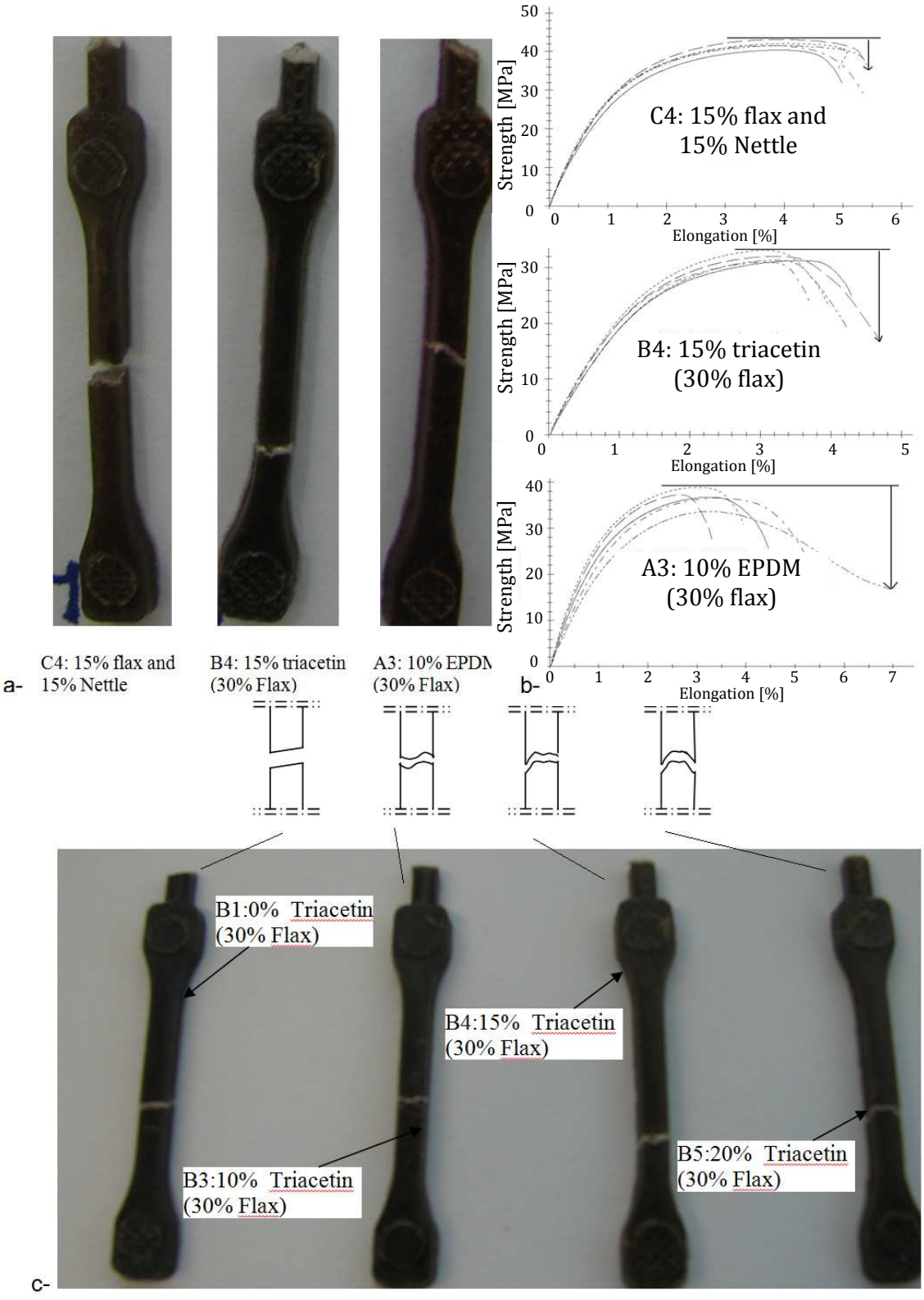


Figure 7-15: Failure features after tension

a- Effect of Nettle, Triacetin and EPDM b- Tensile curves c- Effect of Triacetin%

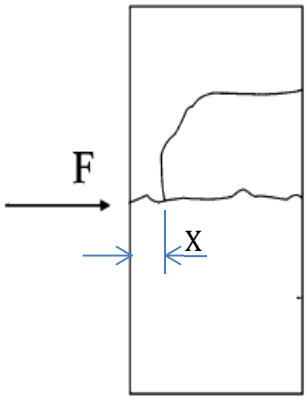


Figure 7-16: Fracture development in Charpy impact samples (Branching schematic)

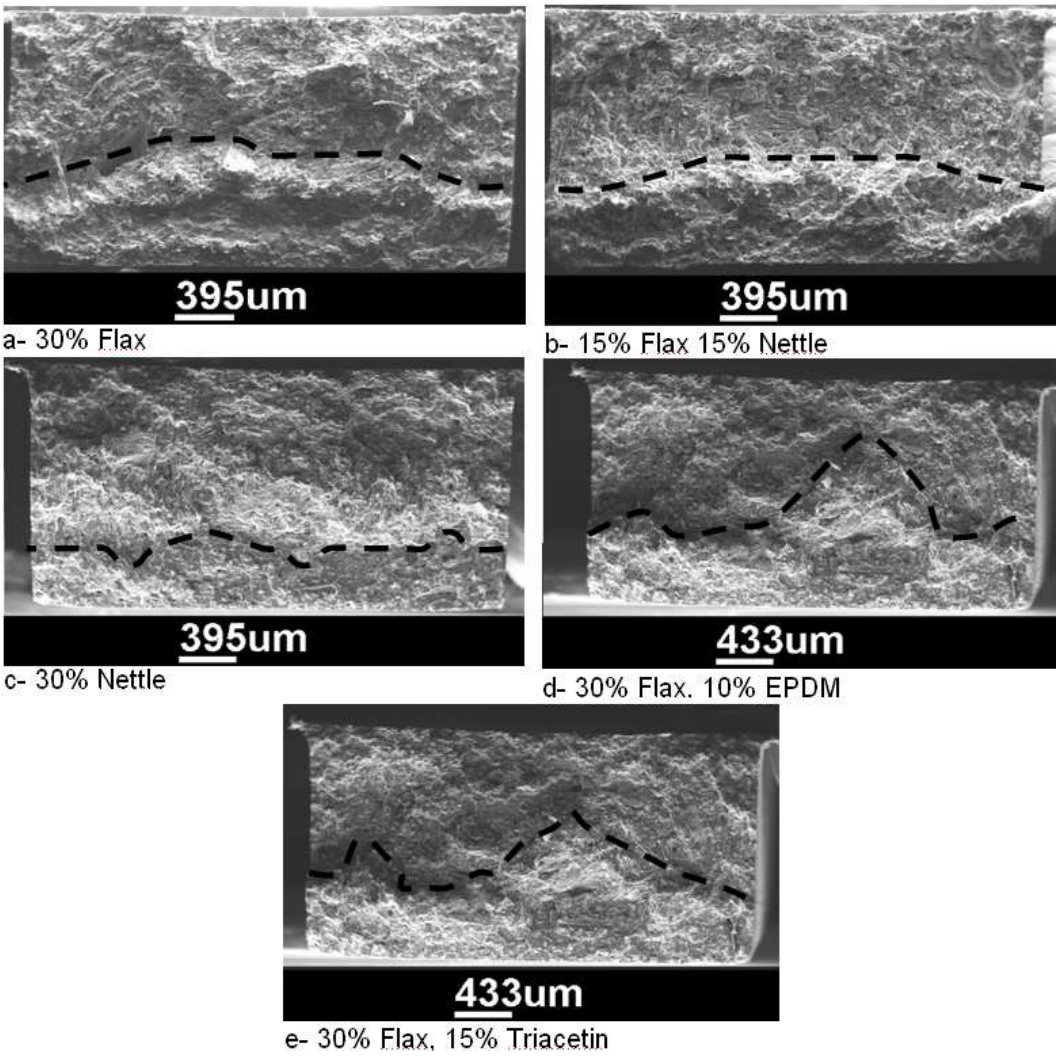


Figure 7-17: Fracture surface of Charpy impact samples a-30% Flax b-15%Flax, 15% nettle c-30% nettle d-30%Flax, 10% EPDM e-30%Flax, 15%Triacetin

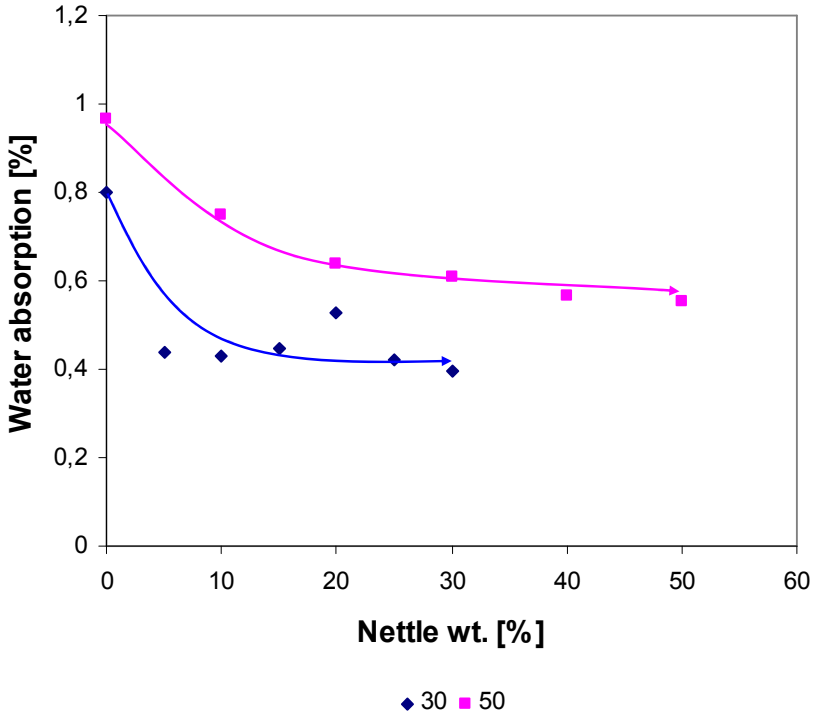


Figure 7-18: Effect of Nettle on composite water absorption for both 30 and 50 wt% (flax+nettle)

Figure 7-19 shows a relative similar behaviour as in Figure 7-18. However, the reduction in water absorption by triacetin is almost the same by the addition of nettle in case of 30% natural fibre. In case of 50% fibre, triacetin decreases the water absorption inconsiderably. This shows that the effect of diameter and hence the capillary effect is significant. The effect of the hydrophilic fibres appears in Figure 7-19 where more absorption is distinguished. Figure 7-20 shows a similar behaviour as in Figure 7-18 and Figure 7-19. Furthermore EPDM is not effective on hindering water absorption for the composites filled with 30% fibres, as in case of triacetin.

7.1.4 Outcomes

Three methods are investigated to improve the impact strength of NFTC. Addition of nettle fibres to the flax fibres in ratio of 1:3 results in an improvement of 20 and 35% for NFTC of 30 and 50% fibres respectively. Addition of EPDM does not reflect an improvement except for the case of 10% EPDM where the impact strength is improved with almost 8%. Meanwhile, addition of triacetin results in negative influence on the impact strength. Regarding other aspects of mechanical properties like tensile strength and E-modulus; Nettle increases the tensile strength, E-modulus and elongation, while EPDM and triacetin decrease the composite tensile strength and E-modulus. Water absorption is reduced efficiently by nettle addition and partially by triacetin in case of composites reinforced with 30% natural fibres.

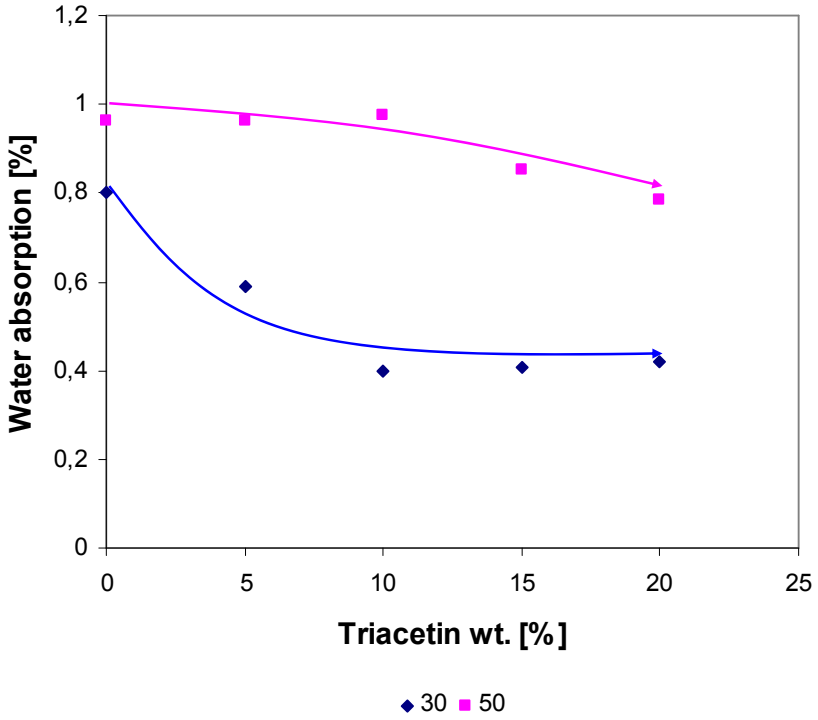


Figure 7-19: Effect of Triacetin content on composite water absorption for both 30 and 50 wt% flax

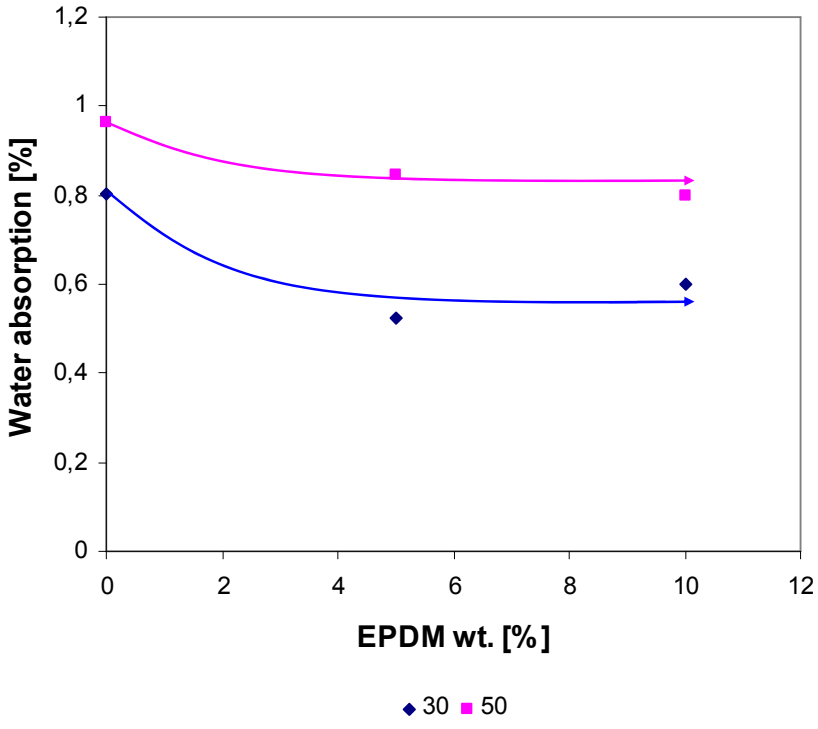


Figure 7-20: Effect of EPDM content on composite water absorption for both of 30 and 50 wt% flax

7.2 Influence of flame retardants in NFTC

7.2.1 Introduction

Natural fibre thermoplastic composites NFTC are recently applied to high added value applications in electronic and automobile industries [Ble99a], [Gar08] Flammability of NFPC is a decisive factor which will define the scope of these composites' application.

The flammability behaviour of natural fibre is governed by lignin and cellulose/hemicellulose as mentioned in 2.6.2. Two contradicting natures in natural fibres are affecting the whole flammability behaviour of the composite. On one side, the aromatic rings present in lignin resist fibre oxidation and lignin produces less volatiles [Cha10a] [Koz08], [Fer02], [Vir12]. On the other side, cellulose supports the flammability process because it produces the volatile flammables [Cha10a], [El-13c]. In other words, increase of cellulose percent promotes the flammability whereas increase in lignin promotes the formation of insulating char [Dit12], [Sua11], [Azw13].

The number of flame retardance studies concerning natural fibre composites is still limited because it depends on the volume of the market of NFPC. Table 7-4 lists some milestones in the application of FR in NFTC.

Table 7-4. Literature survey of applying FR in NFTC

#	Source	NFTC	FR	Remarks
1	Helwig et al. [Hel00]	Press moulded PP sheets with flax bundles (12.5-40%)	No FR is used	cone calorimetry tests for NFTC characterisation without FR. The addition of fibers, especially in the amount of 30%, resulted in a significant decrease of such an important parameter as heat release rate (HRR) peak
2	Le Bras et al. [Le 05]	PP/flax in 60:40 system	Ammonium polyphosphate (APP) APP synergised with entaerythritol (PER) and melamine (MEL)	APP only was not enough to reach any of the UL94 ratings. Synergism of APP with PER and MEL satisfied the V-0 conditions.*
3	Schartel et al. [Sch03]	PP/flax in 70:30 system	APP in 25% Expandable graphite (EG) in 15-25%	He reached HB level V-1 level with 25% EG.
4	Sain et al. [Sai04]	PP/(Sawdust-Rice husk) in 50:50. The mix of sawdust and ricehusk is 50% with different ratios	The hydrated inorganic metals. $Mg(OH)_2$ is selected due to its higher thermal stability compared to ATH which is limited to 204°C [Wei08]. $Mg(OH)_2$ of 20-25 wt.-% in addition to zink borate (ZB)	The horizontal flame speed was reduced by almost 50% at 25% $Mg(OH)_2$ in case of sawdust and limiting oxygen index (LOI) of 35 is also attained.**

			or boric acid at 5% for the PP/Sawdust and PP/rice husk.	

**Unfortunately, the corresponding results of mechanical properties were not described.

** The reason of using only 25% of $Mg(OH)_2$ in NFPC is attributed to the need of natural fibre and polymer. Use of FR in high contents in addition to 30-50 wt.-% of natural fibre will leave only a small share for the polypropylene matrix to bind the composite constituents.

In this part of the study, different flame retardants (Inorganic hydrates, halogenated, halogen-free intumescent, etc.) are applied to get more applicable products, bearing in mind that the implementation of such retardants results in another problem which is the drop of the corresponding mechanical properties [Sai04]. Therefore, a comprehensive study for different FR classes and fibre types is necessary to characterise NFTC regarding both mechanical and flame resistance.

7.2.2 Experiments for applying different flame retardants

The materials used in this study as mentioned in section 3.2 are as follows: Natural fibres of flax, jute, hemp and sisal were supplied by Sachsenleinen- Germany as listed in Table 3-1. They are treated with NaOH 5% solution for 24 hours and neutralised. The fibres are then left overnight in air and afterwards dried for 24 hours at 105°C. Polypropylene DOW H 734 52 RNA (Dow) is used as matrix. Maleated anhydride grafted polypropylene matrix MAPP is used as a coupling agent in ratio of 1:10 to the natural fibre weight. The used FRs in this study are inorganinc metal hydrate $Mg(OH)_2$, The synergetic effect of nano clay (Sodium montmorillonite) and intumescent FR as ammonium polyphosphate Exolit AP-766, supplied by Clariant, is investigated. Decabromodiphenyl oxide DECA alone and with Antimony trioxide Sb_2O_3 is also studied. Table 7-5 shows the compositions of the trials in this study. All FRs except AP-766 are supplied by Sigma Aldrich.

Table 7-5. Different groups of added flame retardants

Group	Fibre	Effect of:	Parameter wt.%
A	30% & 50% Flax	$Mg(OH)_2$	0, 20, 30
B	30% Flax	AP-766	20, 22, 24, 26, 28
C		AP-766+ nanoclay	20 0,1,2,3,4,5
D		DECA+ Sb_2O_3	20, 22, 24, 26, 28 6
E		DECA+	24

		Sb_2O_3	3,6,9,12
F	30% (Flax, Hemp,Jute, sisal)	$Mg(OH)_2$	30%
G		AP-766	24, 26, 28
H	30% Flax	$Mg(OH)_2$+ nanoclay	30 5

7.2.3 Processing and Testing

Compounding is carried out using 600P kneader Haake Rheomix at 180°C/ 50 rpm for 15 minutes. FRs and/or synergism material are added to the mix of PP + MAPP + Fibre. The compounded material is cut by a mechanical shredder to small granules which are then dried overnight and then processed for the following tests:

Mechanical tests: injection moulded at a temperature pattern of 185-190-195-200°C using Allrounder 220C 600-250, Arburg, Lossburg, Germany to tensile samples 1BB size according to ISO 527-2 and impact samples of according to ISO 179-1. Samples of mechanical testing are conditioned at 23°C/50% relative humidity for at least 88 hours according to ISO 291 for test room conditions. Tension tests were made using Zwick 2.5 kN tensile machine. Test is conducted and evaluated according to ISO 527-1.

Flammability tests: UL94 samples are either injection moulded or hot pressed when samples are repeatedly agglomerating and causing stoppage in injection particularly with the high FR loading in the group A of 50% Flax.

7.2.4 Results and discussion

A- Flame resistance results

Figure 7-21 illustrates the UL94 values of all groups listed in Table 7-5. It is obvious that $Mg(OH)_2$ is not sufficient till 50 wt% to reach any V-class. However it helps in reaching HB class. Even only 20% of $Mg(OH)_2$ is enough for 50% flax samples to get the HB class. Nanoclay does not show significant synergism within the qualitative test of UL94.

Intumescent AP-766 proved its efficiency starting from 24% level to get V2 class till V0 at 26%. Smoke evolves slightly with 20% AP-766 which is not the case with 28%. No reddish glowing points remain obvious after the test.

Nanoclay shows significance with AP-766. 3% and 5% clay with 20% AP 766 make the rating jump to V1 and V0. Results of nanoclay drop at 4% clay. This is probably due to poor mixing quality which fails to ensure good dispersion/ exfoliation of the nanoclay in the matrix/fibre compound. This can be attributed to low applied shear rate [Bag08]. On the other side, high shear rates cause fibre damage and reduce the fibre

aspect ratio which is the responsible of load transfer efficiency. Therefore nanoclays are added before fibres' addition. This strategy represents a challenge for the already mixed commercial natural fibre polymer granules. In other words, an optimised mixing strategy is required for good mix without fibre damaging.

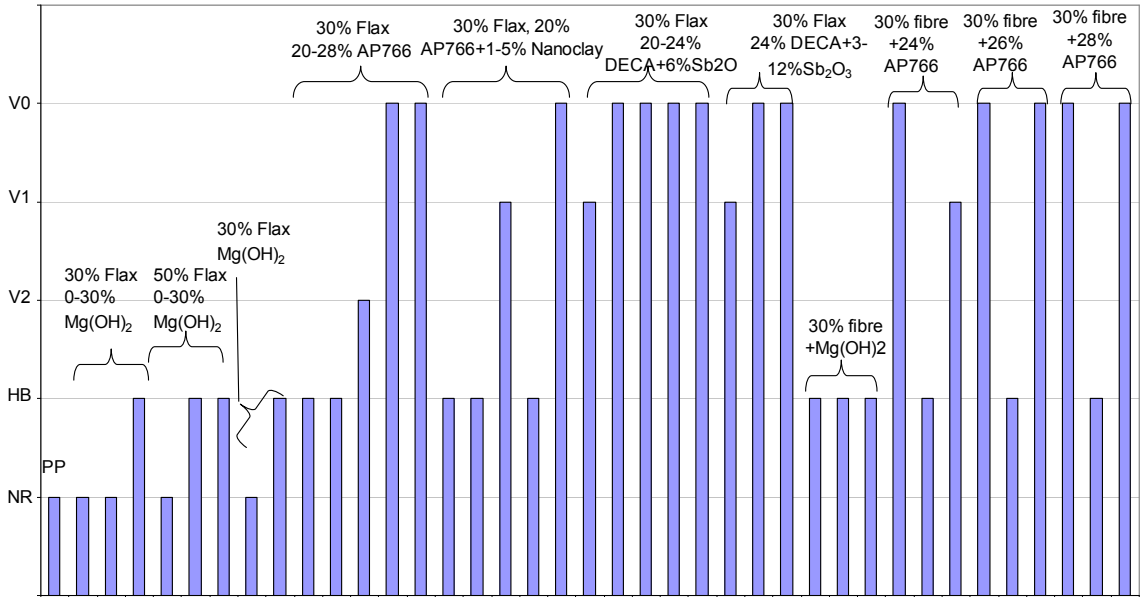


Figure 7-21: UL94 results of all groups

DECA also performs successfully with 30% flax at all tried contents in synergism with 6% Sb_2O_3. However the synergism of Sb_2O_3 is obvious because the UL94 class drops to V1 when only 3% of Sb_2O_3 is applied. Effect of using different fibres shows insignificance. It is worthily noted that reddish glowing point remains for seconds after finishing the test in case of DECA application. Not only this, but evolving smoke is also observed.

The type of fibre shows significance where flax and hemp fibres have higher class. Jute has failed to pass the V0 class and sticks to HB level. Sisal, the leaf fibre, shows also a slightly better behaviour than jute but worse than flax and hemp. Flax and hemp show the fastest distinguishing time after the removal of the flame source. Of course $Mg(OH)_2$,does not show the fibre type significance because its amount is not sufficient even for flax and hemp.

B- Mechanical testing results

Group A shows that the $Mg(OH)_2$ affect the strength negatively due to its heavy loading, as shown in Figure 7-22. 32% drop in strength for the 50% flax group is measured whereas only 10% drop in UTS is found in 30% flax composites.

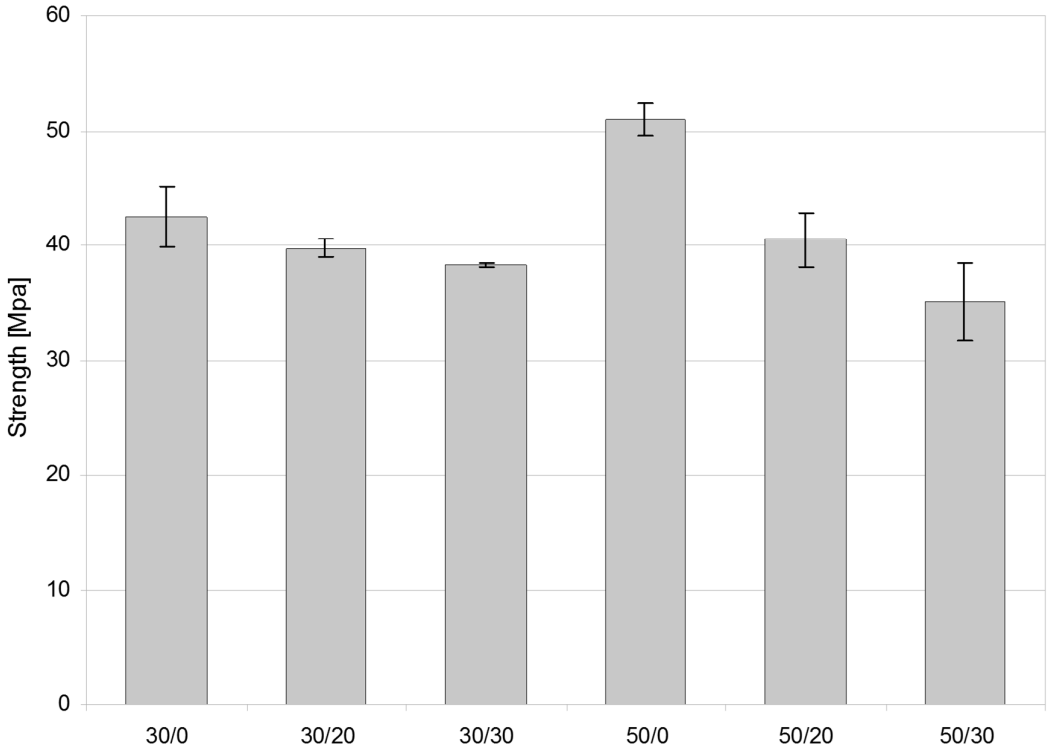


Figure 7-22: Effect of Fibre wt.%/ $Mg(OH)_2$% on UTS

Figure 7-23a shows that the effect of AP-766 (group B) on the strength of the 30% Flax composite. The drop in strength is close to that resulted by $Mg(OH)_2$%. The drop is almost 25% at 20% AP-766. The behaviour of AP-766 is not following a decreasing linear trend line. In Figure 7-23b, nanoclays (group C) show a reducing effect for composite UTS in an approximate linear way. 5% nanoclays lead to almost 29% loss in strength. The same discussion can imply on group H for nanoclays with $Mg(OH)_2$%.

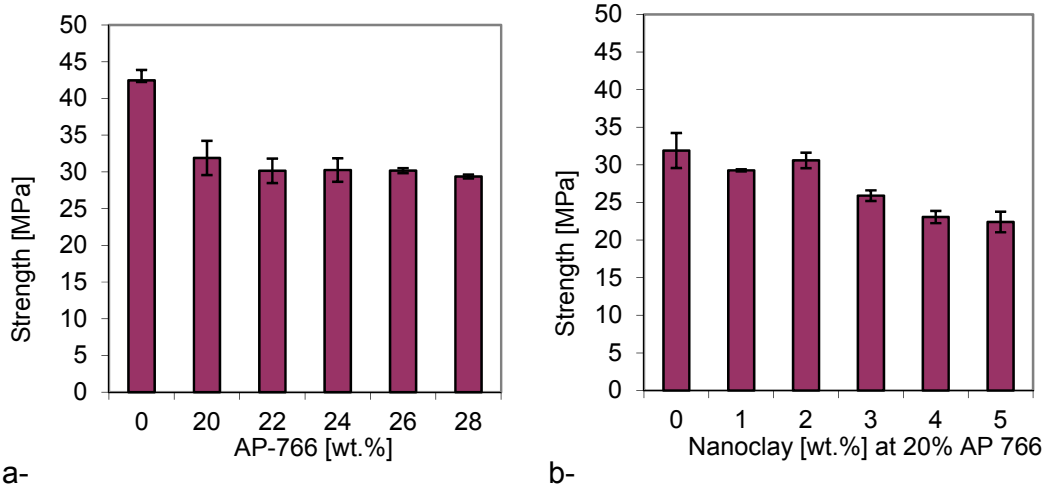


Figure 7-23: Effect of a- AP 766 b-nanoclay wt.% on UTS

Figure 7-24a shows that the effect of DECA is too small. Strength decreases only 14% at maximum level of DECA used which is 28%. Also the effect of the synergist antimony trioxide (group D) as shown in Figure 7-24b is insignificant. However the healthy restrictions (2002/95/EC) on the assumed toxic nature of DECA should be considered.

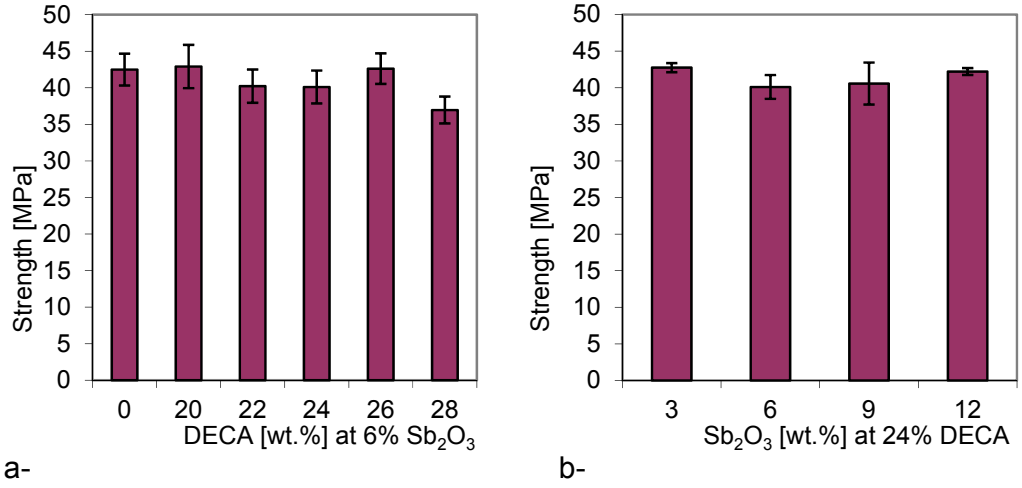


Figure 7-24: Effect of a- DECA b-Sb_2O_3 wt.% on UTS

Figure 7-25a shows the effect of fibre type at 30% Mg(OH)2 on strength. Only sisal has a little bit strength less than those of the other fibre types of flax, hemp and jute. Figure 7-25b shows that jute composites have higher UTS than the others. The gradual increase of AP-766 shows insignificance except for jute. Considering the reference strength of composites (without FR appearing as solid bars), the effect of AP-766 on all fibre types is the same. That is different from what noticed with magnesium hydroxide, Figure 7-25a, where only sisal and jute are heavily affected more than flax and hemp.

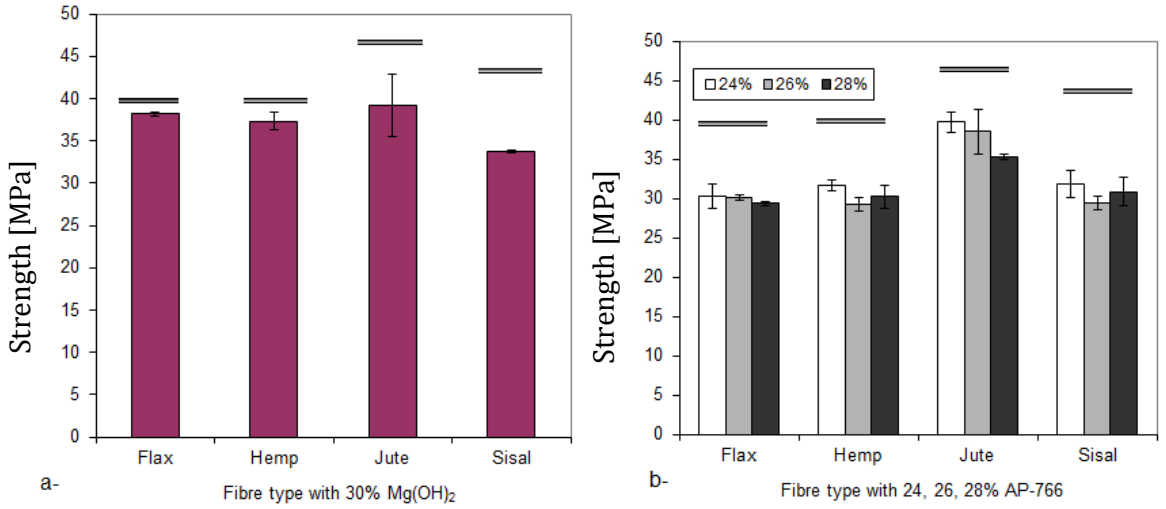


Figure 7-25: Effect of fibre type on UTS a- Mg(OH)2% b-24% AP-766 c-26% AP-766 d-28% AP-766

7.2.5 Outcomes

A survey for different FR on different fibre types of NFTC is carried out. Flame resistance as well as the resulting mechanical properties are considered. DECA or DECA/ Sb_2O_3 show the best result. But considering the healthy regulations, AP-766 has the next best performance starting from 26% to reach V0 class but with 29% loss in UTS. Nanoclays affect significantly where 3% of nanoclays with 20% AP766 reaches the V0 class. The mineral FR Magnesium hydroxide, with its high thermal stability and good ecological impact, needs thorough studying to attain better classification. However for HB-class, it can be considered with a loss in UTS around 30%. To summarise both the flame retadance and mechanical properties results and the effect of the selected FR, Figure 7-26 shows a material selection chart which combines both UL94 results with the tensile strength. It can be helpful in achieving a simple selection tool.

Considering the fact that DECA is out of the selection spectrum due to the IEC regulation and based on the preliminary results presented in the previous section, the use of the mineral FR (alone or in synergism with ammonium polyphosphate) is very attractive and need further study as shown in the following section 7.3.

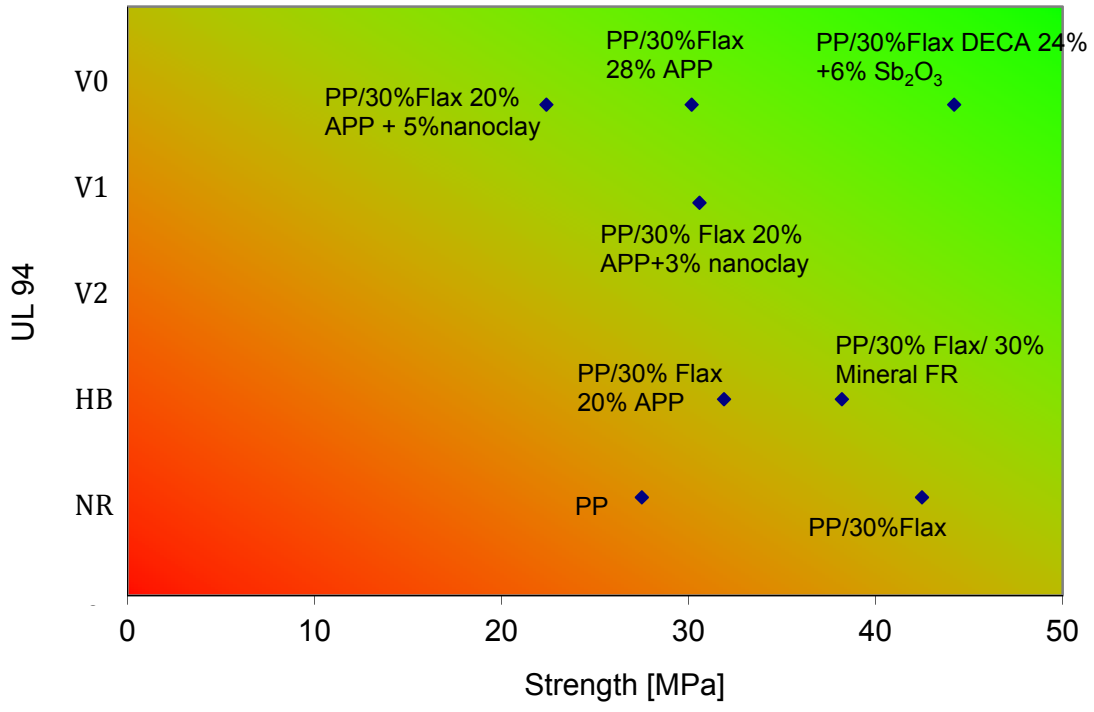


Figure 7-26: Selection chart of FR type regarding the desired flame retardance level and the mechanical property

7.3 Optimisation of flame retardant content regarding mechanical properties for NFTC

7.3.1 Introduction

As mentioned in the previous section, mineral flame retardants and especially the mineral inorganic hydrates (such as magnesium hydroxide and Aluminium trihydrate ATH) are promising for further studies. However, they result in another problem which is the drop of the corresponding mechanical properties [Sai04]. The flame retardant additives to NFTC reduce the share of the host polymer matrix which is responsible of binding the composite constituents together. Hence, the tensile strength of NFTC is decreased.

Flame retardation using ATH is implemented through a physical mode of action. Physical mode flame retarding mechanism takes place either by cooling or by formation of a protective pyrolysis layer. Flame retardation by cooling is achieved by endothermic reactions as shown in Equation 7-3 in which the metallic hydroxides degradation is accompanied by water release. In the other case of flame retardation, a protective pyrolysis layer is formed when using phosphorous as an additive [Koz04], [Fin04]. This means that ATH acts as a heat sink when it is exposed to flame.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$$

Equation 7-3

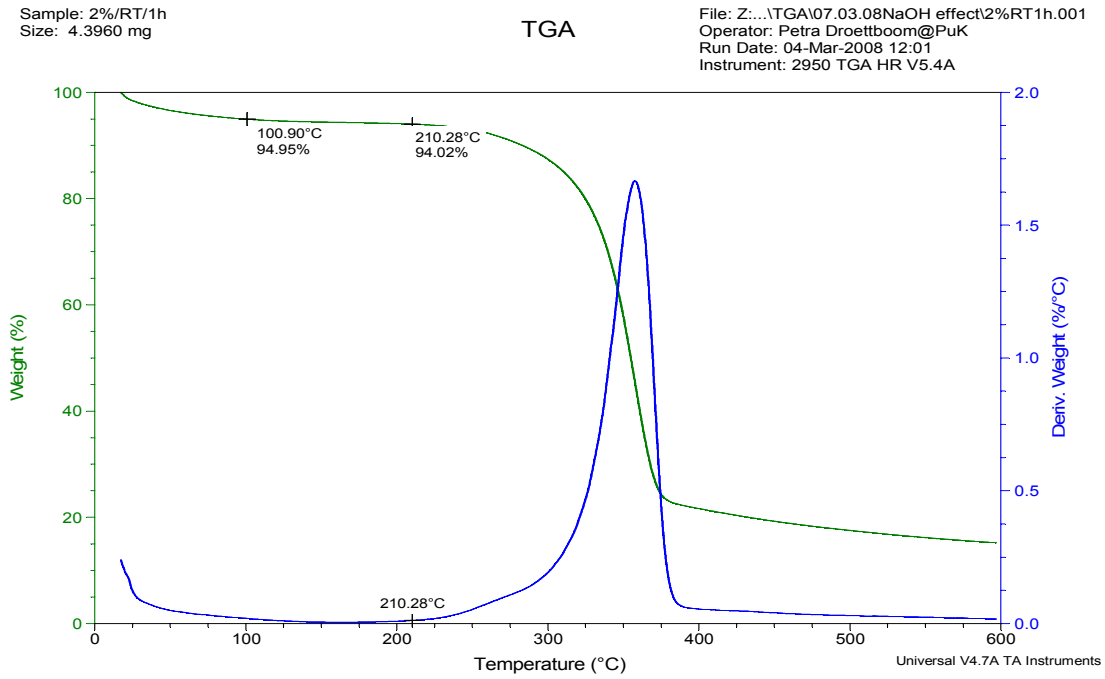
In addition, ATH is characterised with its smoke suppression. This advantage of smoke suppression is necessary in case of adding synergism with phosphate FR because phosphate FR has a drawback regarding smoke [Che15]. ATH addition represents almost 75% of the flame retardance industry for the polyolefines [Wei08]. This is attributed to the possibility of reaching the V-0 rating in UL94V test.

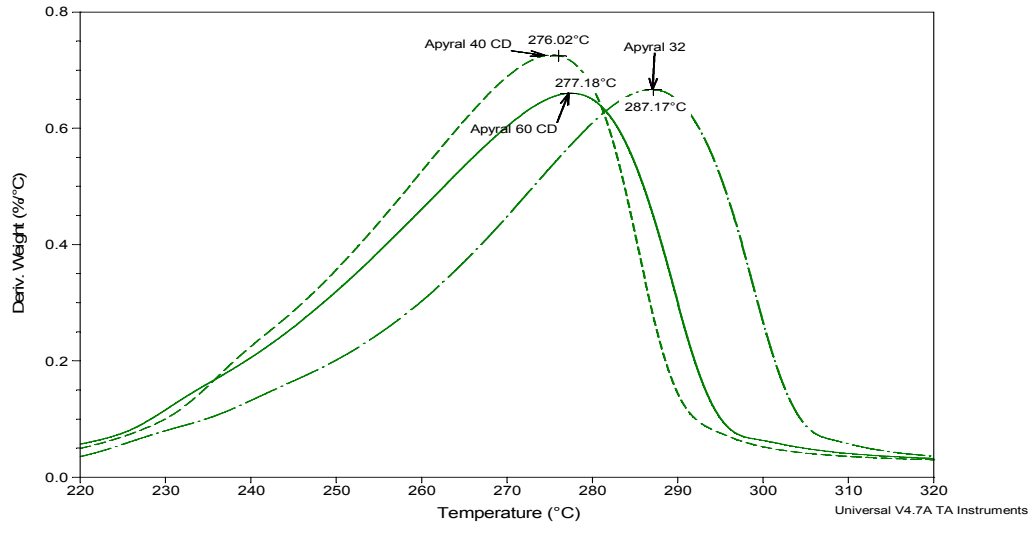
ATH (specific gravity of 2.42) provided by Nabaltec company, as mentioned in Table 3-4, is used. According to the company recommendations, 67 wt.-% of ATH is necessary to reach UL94 V-0 condition with 3.2 mm thickness of PP sample. The size of ATH particles defines the flame retardance behaviour. The higher the specific surface area applied, the better the flame retardance efficiency is. For flax fibres, the processing temperature is recommended not to exceed 200°C to avoid excessive thermal degradation and weight loss of both flax and ATH as shown in Figure 7-27.

PP/flax composites are characterised by high total heat release (THR) compared to glass fibres but slow glowing fire, compared to other types of natural fibres like sisal and jute [Koz08].

This work is assigned to explore the possibility of using ATH with flax / PP composite system. The aim of this work is to maintain the amount of FR to the minimum in order to allow the sufficient amount of PP to bind the natural fibre and the FR. Preserving the mechanical properties of NFPC is also considered. In other words, a compromise has to be investigated to have a V-0 NFPC with minimal mechanical property loss.

a-





b-

Figure 7-27: Thermal gravimetry test of a- alkalinised flax fibre b- ATH with different particles' sizes

7.3.2 Experimental Work

Flax fibres (Sachsenleinen- Germany) are treated and combined with PP and MAPP. MAPP does not serve only as a coupling agent but it hinders also the agglomeration of ATH particles [Ris05]. Two groups of two different ratios between flax and Polymer namely 70:30 and 50:50 are manufactured. The used FR is Apyral 60CD with specific surface area of 6 m²/g and median size of 1 µm. The FR content in the composite recipe is kept constant at 60 wt.-% based on PP matrix (150 phr according to the manufacturer recommendation). Samples' numbers used in investigating each parameter are listed after the parameter name.

Compounding is carried out using co-rotating screw extruder (L/D=40). Where PP and MAPP are fed through the hopper and the flax bundles cut to 10 m length and inserted from the extruder side. The temperature pattern is 180-190-190-200-210-220-230-230 °C from input to output zones. The compound is then shred mechanically and re-mixed with FR using 600P kneader Haake Rheomix at 180°C, 50 rpm for 15 minutes. Kneading time is exceeded to ensure good distribution of ATH at just 50 rpm and not 200 rpm as recommended by Cardenas et al. [Cár13]. The investigated parameters are as following:

- Weight ratios of flax:PP are 30:70 and 50:50 as shown in Table 7-6.
- FR content is investigated at lower percentages than the recommended value of 60 wt.-% namely 0, 30, 40 and 50 wt.-%.

The compounded material is cut again by a mechanical shredder to small granules. These granules are dried overnight at 105°C and then processed as preparation for the following tests:

I. Mechanical tests: Granules are injection moulded at a temperature pattern of 185-190-195-200°C using Allrounder 220C 600-250, Arburg, Lossburg, Germany to tensile samples 1BB size according to ISO 527-2 and impact samples of according to ISO 179-1. Samples of mechanical testing are conditioned at 23°C/50% relative humidity for at least 88 hours according to ISO 291 for test room conditions. Tension tests were performed using Zwick 2 kN tensile machine. Test is conducted and evaluated according to ISO 527-1.

II. Flammability tests:

a. Cone calorimeter testing: At least three samples are required. Granules are press moulded to 100*100*3 mm^3 at 10 bars and 200°C for 15 minutes before cooling under pressure application. These values of temperature, pressure and time are found to be suitable for getting homogeneous and well bonded samples. Up to four samples can be manufactured at the same time in the mould with insertion of 100*100*1 mm steel sheet spacers sprayed with Teflon to facilitate sample demoulding.

b. UL94 test: Samples are either injection moulded or cut directly from the press moulding samples. Dimensions of UL94 samples are 125*12.5*3 mm^3. The test is carried out according to IEC/DIN EN 60695-11-10 and -20 standard.

c. LOI test: LOI test measures the required oxygen concentration required to support the flame sustainability. Samples of type A (125*6.5*3 mm^3) are injection moulded. The test is carried out using Dynisco equipment. Evaluation is done according to the the instructions of the equipment manufacturer based on ASTM D-2863.

Table 7-6. Composition of 30:70 Flax/Polymer group (samples 1-7) and 50:50 group (samples 13-19)

Sample #	FR type	Polymer* [wt.-%]	Flax [wt.-%]	Flax to Polymer ratio	FR ATH [wt.-%]	Synergism AP-422 [wt.-%]	Synergism Zinc borate [wt.-%]
Particle size							
1	--	70	30	30:70	0	0	0
2	APYRAL 32	28	12	30:70	60	0	0
3	APYRAL 40CD	28	12	30:70	60	0	0
4	APYRAL 60CD	28	12	30:70	60	0	0
FR content							
1	--	70	30	30:70	0	0	0
5	APYRAL 60CD	49	21	30:70	30	0	0
6	APYRAL 60CD	42	18	30:70	40	0	0
7	APYRAL 60CD	35	15	30:70	50	0	0
4	APYRAL 60CD	28	12	30:70	60	0	0
Particle size							
13	--	50	50	50:50	0	0	0
14	APYRAL 32	20	20	50:50	60	0	0
15	APYRAL 40CD	20	20	50:50	60	0	0
16	APYRAL 60CD	20	20	50:50	60	0	0
FR content							
13	--	50	50	50:50	0	0	0
17	APYRAL 60CD	35	35	50:50	30	0	0
18	APYRAL 60CD	30	30	50:50	40	0	0

19	APYRAL 60CD	25	25	50:50	50	0	0
16	APYRAL 60CD	20	20	50:50	60	0	0

*Polymer means the mix of PP with MAPP

7.3.3 Mechanical Testing Results and Discussion

The mechanical results of the reference samples of composites (without FR) namely samples 1 and 13 are shown in the net diagram, Figure 7-28a. Figure 7-28b shows the mechanical properties of samples 4 and 16 (same samples 1 and 13 after the addition of 60% ATH). Two main observations are found:

- As expected, higher flax content of 50% results in higher E-modulus and strength whereas the elongation is almost 50% reduced from 4% to 2% and thus results in reduction in the overall impact strength.
- The addition of FR at high loadings affects the mechanical properties negatively.

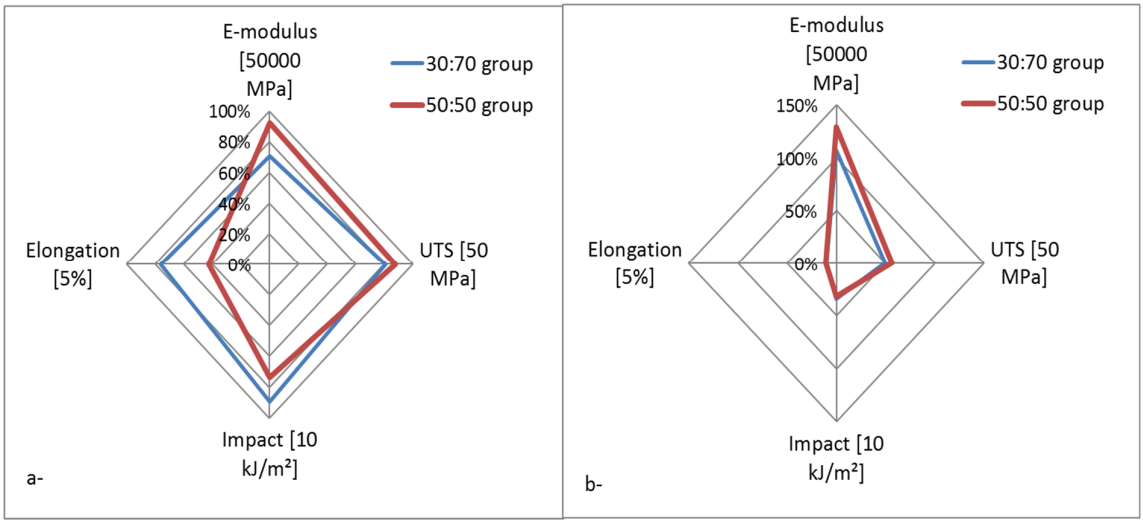


Figure 7-28: Mechanical properties of 30:70 and 50:50 Flax:Polymer composites a- without FR b-with FR

As shown in Figure 7-29, in comparison to the composites without FR, the E-modulus of the 60 wt.-%ATH filled composites is enhanced by 46% and 40% for the 30:70 and 50:50 groups respectively. However, the effect of the particle size is insignificant in this group of experiments. This contradicts the expectations where it was anticipated that the finer the ATH applied, the higher is the influence on the mechanical properties. This could be attributed to the use of a low shearing rate in compounding [Cár13].

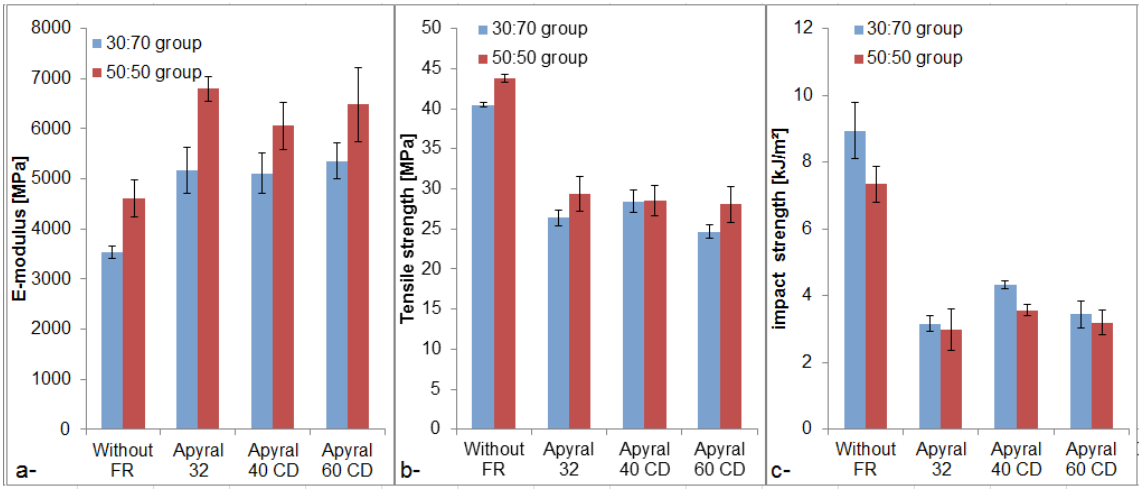


Figure 7-29: Effect of particle size on the mechanical properties of 30:70 and 50:50 Flax : Polymer composites after addition of 60% FR a- E-modulus, b- tensile strength, c- Impact strength

As shown in Figure 7-29, the drop in strength by increasing the ATH content encourages the investigation of lower loading of ATH. Figure 7-30 shows the effect of different FR contents. 50:50 group shows both higher impact and strength in comparison to the 30:70 group. It is clear that the linear trend line changes its trend at 40%. For 30:70 case, the strength decreases slightly by 12.5 at 40% ATH then decreases further by 17% at 50% ATH and then drops by 40% loss at 60% ATH. For the 50:50 case, the strength similarly decreases slightly by 7% at the 40% ATH, then drops by 20% at 50% ATH and finally by 37% at 60% ATH. This behaviour of changing the linear trend at almost 40% ATH is also obvious in the other measured properties (E-modulus, impact strength and elongation). This result seems promising that the tensile strength loses only about 10% after the addition of the 40% ATH. Saving 20% of ATH will increase automatically the share of the PP polymer to bind with both natural fibres and the FR. However, it is needed to check the performance of the flammability test of the NFPC at 40 wt.-% loading of ATH.

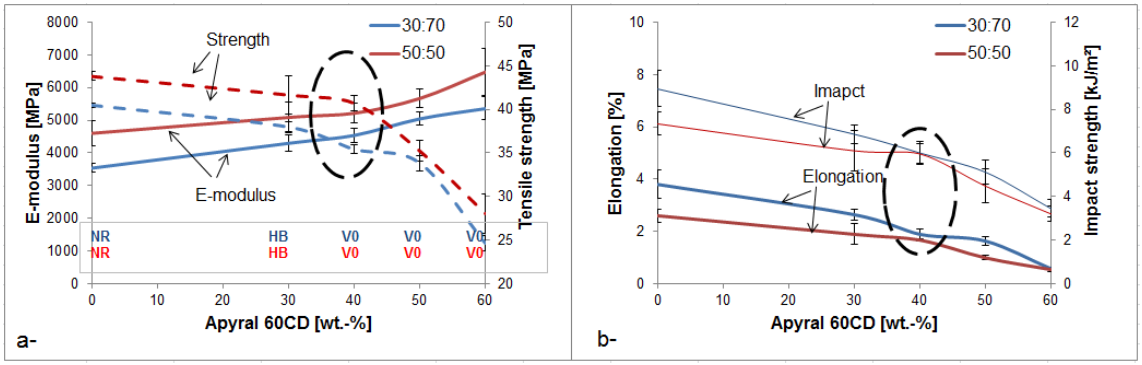


Figure 7-30: Impact/ strength of 30:70 & 50:50 groups at different ATH%

7.3.4 Flammability Testing Results and Discussion (Cone calorimetry)

The cone calorimetry results are summarised in Table 7-7. The abbreviations are as follows: peak heat release rate (PHRR), Maximum average rate of heat emitted calculated from HRR-Time per m² (MARHE), total heat released per m² (THR), total smoke released normalised for the surface area of the specimen (TSR), time to stable ignition of at least 5 s (TTI), time to peak heat release rate (TTPHRR), time to flame distinguishing (TT flame out) and mass loss in comparison to the original value (Total mass loss). Table 3 lists the results of the other flammability tests namely the LOI and UL94.

For the sake of comparison with literature, the cone calorimetry of sample 1 is compared with 30/70 of flax/PP reported by Helwig [21]. Bearing in mind that the sample preparation technique is different, the values of PHRR, THR, TTI and TT flame out by Helwig [28] are almost 450, 125, 39 and 480 while in Table 7-7 the corresponding values are 509, 121.3, 22 and 773 respectively. The values especially PHRR and THR are close to each other.

Table 7-7. Cone calorimeter results of the investigated composites

Sample # and Composition	PHRR [kW/m²]	MARHE [kW/m²]	THR [MJ/m²]	TSR [m²/m²]	TTI [s]	TT PHRR [s]	TT flame out [s]	Total mass loss [%]
1- (30/70)0%	509.0	368.3	121.3	1341.5	22.0	121.7	773.0	100.0
2- (30/70)60%Apyral 32	182.5	123.6	62.9	351.5	45.0	118.3	600.0	63.8
3- (30/70)60%Apyral 40CD	191.6	119.3	64.2	413.5	51.0	188.3	591.0	61.1
4- (30/70)60%Apyral 60CD	197.3	118.1	56.9	450.7	60.0	313.3	590.7	62.7
5- (30/70)30%Apyral 60CD	350.8	226.9	95.8	892.0	24.3	80.0	599.0	79.1
6- (30/70)40%Apyral 60CD	247.5	173.0	99.7	870.1	38.0	281.7	827.0	75.1
7- (30/70)50%Apyral 60CD	197.0	131.3	86.8	734.0	58.3	363.3	917.3	69.3
8- (50/50)0%	502.3	345.4	116.6	1212.9	29.0	185.0	750.0	97.2
9- (50/50)60%Apyral 32	185.1	102.1	69.9	515.2	92.3	355.0	801.7	63.6
10- (50/50)60%Apyral 40CD	169.2	90.6	73.7	558.9	125.3	418.3	867.7	60.4
11- (50/50)60%Apyral 60CD	179.7	88.2	68.8	622.8	171.0	441.7	842.7	59.9
12- (50/50)30%Apyral 60CD	278.5	194.9	104.1	1005.0	47.0	227.5	931.0	79.9
13- (50/50)40%Apyral 60CD	253.2	162.8	97.0	928.2	62.3	320.0	824.0	73.1
14- (50/50)50%Apyral 60CD	214.2	121.0	77.1	688.4	77.0	308.3	824.3	67.1

Figure 7-31a shows the cone calorimetry main results concerning the 30:70 and 50:50 composites (samples 1 and 13) where no FR is applied. After the application of FR, the cone calorimetry indices are shown in figure 7b. The following observations are noticed:

- The improvement in flame retardance by FR application is clear between figure 7a and figure 7b.
- Difference in flammability behaviour of both composite groups (30% and 50%) increased. The 50:50 group has more delay in TTI, slightly higher total heat release THR as well as more smoke release TSR. Similarly, the values of TTPHRR and TT-flame-out for the 50:50 composites are higher than those of 30:70 composites. However the delay of TT-flame-out for the 50:50 samples seems unexpected because low polymer share is inside. This can be explained by the natural fibre role in burning as the fibres support the burning process. The role of fibres is also ensured by higher smoke release in case of 50:50 group. But generally, a composite with increased flax content has relatively better flame retardance behaviour which matches with previous findings [El-13c].

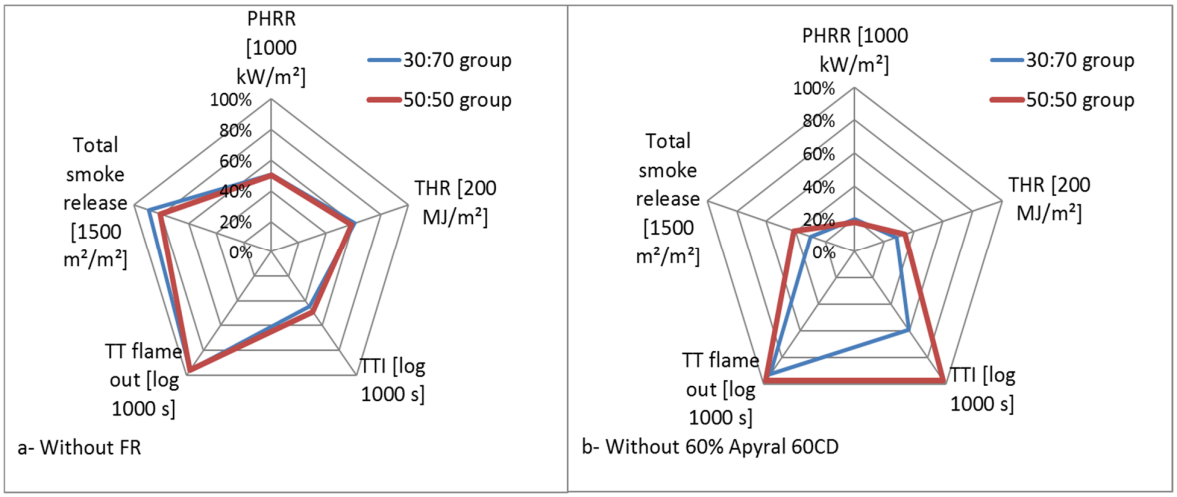


Figure 7-31: Cone calorimetry results of 30:70 and 50:50 Flax : Polymer composites

a- without FR b- with FR

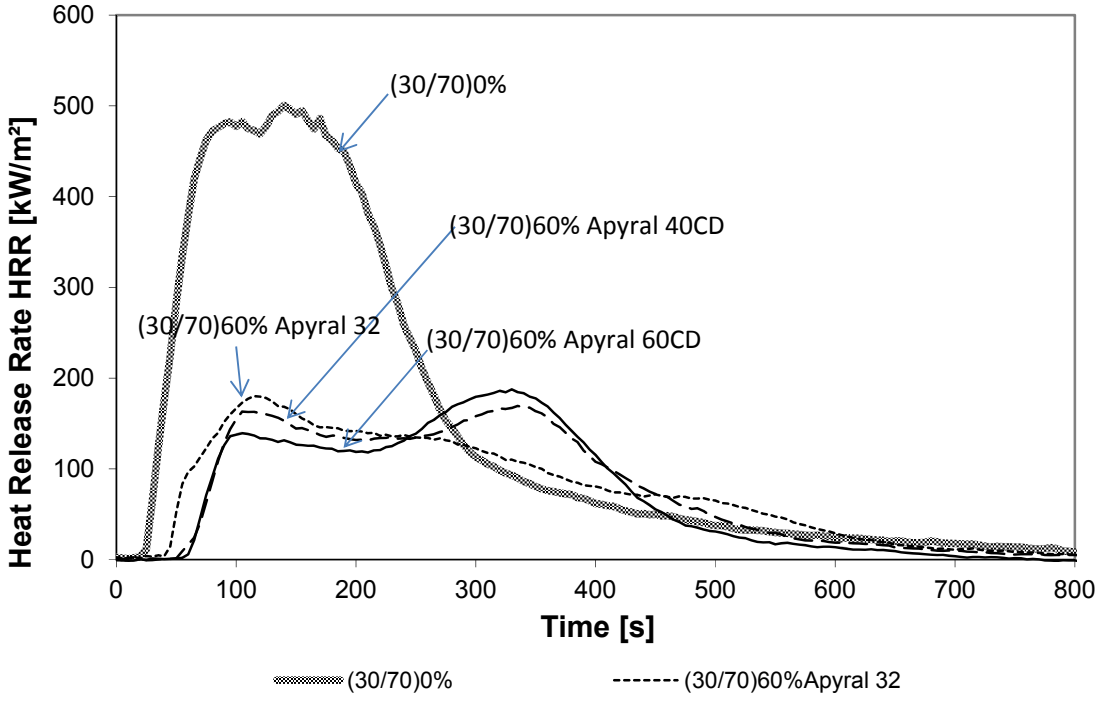
Figure 7-32a presents the HRR curves of the 30:70 group. The non-filled sample with ATH has a rapid time to stable ignition TTI of 22 s. The total heat released per m² THR value has a maximum value of 121.3 MJ/m². The use of the coarse ATH particle, Apyral 32, prolonged TTI to 45 s and reduced the THR to 62.9 MJ/m².

Effect of ATH particle size on PHRR is clear where PHRR is reduced with the use of ATH filler from 509 to almost 182 kW/m² at the coarse size of Apyral 32. Then it increases again to 197.3 kW/m² after the application of Apyral 60CD. Similarly, TSR is reduced from 1341.5 to 351.5 m²/m² after using the coarse Apyral 32. Then TSR slightly increased again to 450.7 m²/m² after using the fine particles of Apyral 60CD.

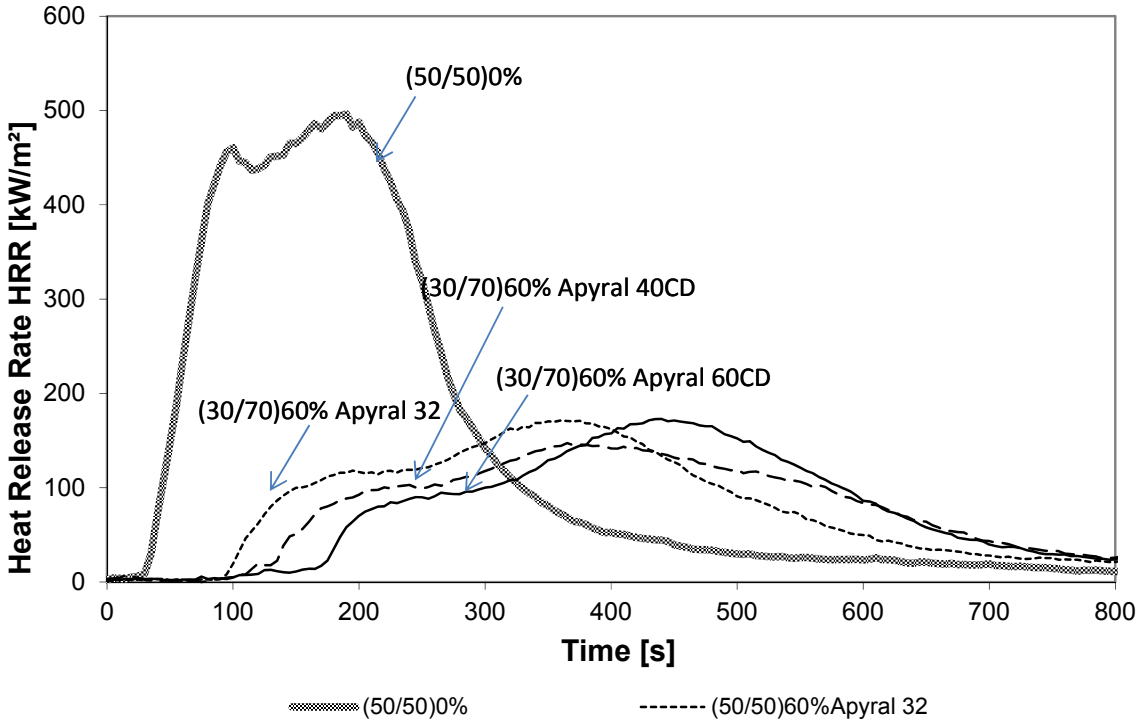
Also as the particles get finer, longer times for getting stable flame TTI is needed. TTI changes from 22 s in case of non FR sample to 45 s with the coarse Apyral 32 and finally to 60 s with the finest ATH Apyral 60 CD. Similarly, the time required for reaching the peak rate TTPHRR is prolonged from two minutes to more than 5 minutes. The increase of the measured index value with the fineness of ATH particle can be attributed to the increased the active area. Hence the heat sink action of ATH as shown in Equation 7-3 is working efficiently with more polymer sites.

On the other side there are other measured indices which decrease with the fineness of the particles. The finer the particle the lower the maximum average rate of heat emitted calculated from HRR-Time per m² MARHE (from 368.1 to 118.1 kW/m²). Also, THR decreases from 121.3 to 56.9 MJ/m² and TTI flame-out (from 12 minutes to 5 minutes). Finally the total mass loss in percent TML decreased from 100% (sample 1 with no FR totally lost its mass) to 63.8% with the coarse ATH then to 61.1% at finer particles.

Same analysis of the ATH particle size can be generalised for the 50:50 group, and Figure 7-32b. The dependence of the cone calorimetry indices on the particle size is even clearer with the 50:50 group. The only exception is TT flame out. This index increased from 12.5 minutes to almost 14.5 minutes at Apyral 40 CD then retreats to 14 minutes with the finest particles of Apyral 60 CD.



a-



b-

Figure 7-32: Effect of ATH specific surface area on HRR a-30:70 group b-50:50 group

Figure 7-33 shows the effect of changing the FR content up to 60 wt% for the both groups of samples. An offset in the HRR curves to right side is observed as a result of increasing the fibre content. Therefore both TTI and TTPHRR increased with the increase of the FR content. TTI increased from 22 s to 38 s and from 29 s to 171 s at 60% FR for the 30:70 and 50:50 groups respectively. Likewise is the behaviour is observed for the TTPHRR. While TT-flame-out fluctuates around 770 s (almost 13 minutes). Thus in turn, the active time of burning (TT flame out – TTI) is getting shorter with the increase of the FR content.

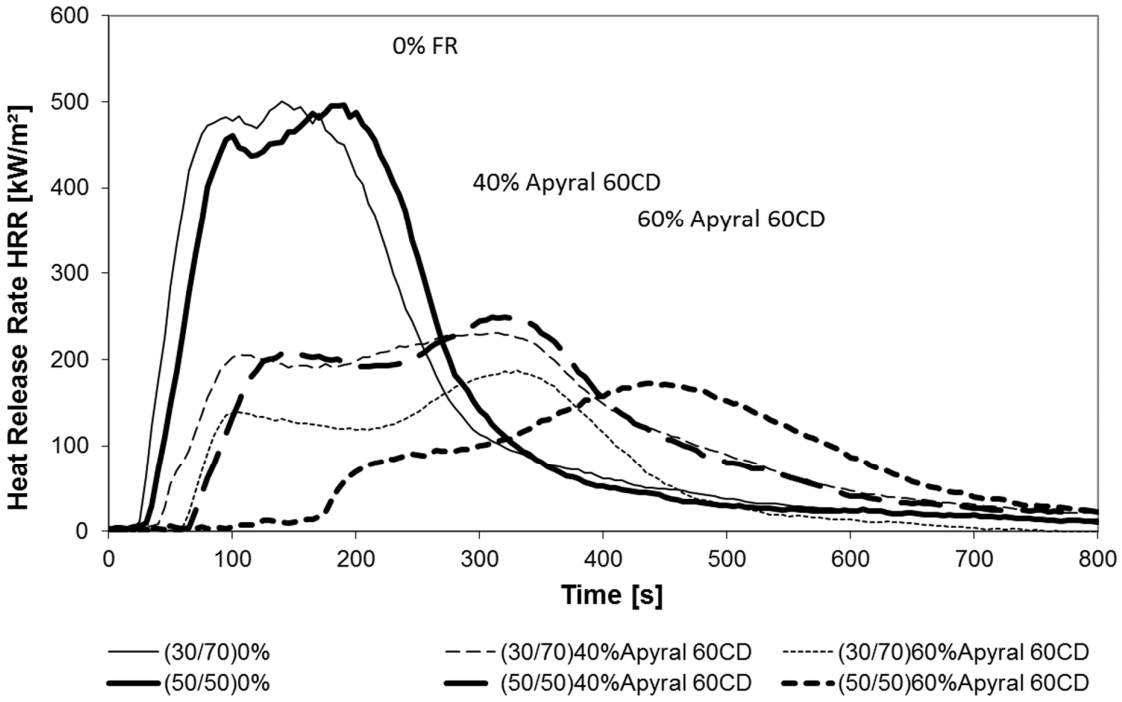


Figure 7-33: Effect of flax content and ATH specific surface area on HRR

Figure 7-34 shows the effect of the Apyral 60CD content on the sample morphology after cone calorimetry test. The grid marks shown on the sample surfaces in some photos are due to the steel grid used in the cone calorimeter test rig which fixes the sample in the required position. More ATH fillers decrease the ash-like features and increase the cohesion features. Figure 12a is more ashy compared to figure 12b. Figure 12c with 40 wt.-% ATH shows the char adheres to the steel grid wire indicating the role of PP matrix that melts and adheres to the grid. The PP afterwards solidifies leaving the white colour because of the ATH. Figure 12d for the 50 wt.-% ATH shows the good cohesion of the sample where the steel grid is easily de-bonded from the sample. Again, the cohesion feature is noticed in figure 12e with 60% Apyral 60CD.

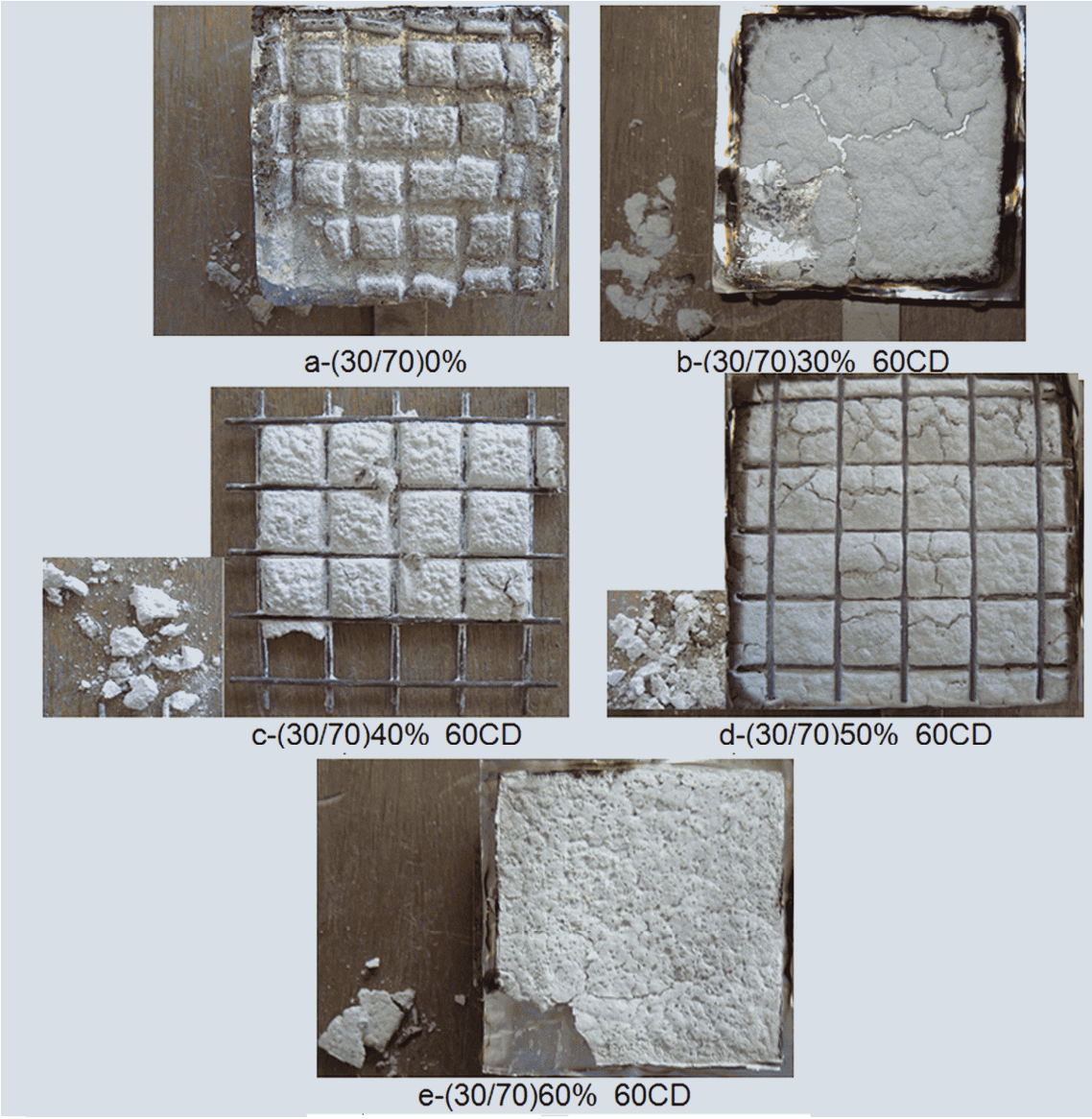


Figure 7-34: Effect of ATH content in the 30/70 group (a-e) on tested samples morphology

7.3.5 Flammability Testing Results and Discussion (UL94 and LOI)

Table 7-8 presents the results of both UL94 and LOI tests. UL94 test as a qualitative test show almost the same results for the two groups of composites except for two cases. All samples with all the investigated particles' sizes reached V-0 class at the 60 wt.-% loading. This means that coarser sizes are required to be investigated to find the critical specific surface area. The results of LOI show almost similar behaviour to the cone calorimeter results. The LOI results did not follow the particle size pattern. This matches the THR from the cone calorimeter. This can be attributed to improper mixing in case of Apyral 60CD.

As shown in Table 7-8, samples 1 and 13 are not rated. 30% ATH improved the rating to HB level. This indicates the role of flax in decreasing the flame aggressiveness.

Starting from 40% ATH, the V-0 rating is achieved. This positive result proves that the content of ATH can be optimised to have more polymer and fibre share.

Table 7-8. Results of UL94 and LOI tests on the composites

Sample	LOI	UL94			
		V-0	V-1	HB* [mm/s]	Not rated
1- (30/70)0%	Not available				
2- (30/70)60%Apyral 32	“”				
3- (30/70)60%Apyral 40CD	“”				
4- (30/70)60%Apyral 60CD	“”				
5- (30/70)30%Apyral 60CD	“”			0.313	
6- (30/70)40%Apyral 60CD	“”				
7- (30/70)50%Apyral 60CD	“”				
13- (50/50)0%	21.8				
14- (50/50)60%Apyral 32	40				
15- (50/50)60%Apyral 40CD	39.4				
16- (50/50)60%Apyral 60CD	39.8				
17- (50/50)30%Apyral 60CD	23.4			0.240	
18- (50/50)40%Apyral 60CD	29.3				
19- (50/50)50%Apyral 60CD	34.6				

* For sample thickness more than 3 mm. HB class is given for horizontal burning speed less than 1.5 inch/min (0.635 mm/s).

7.3.6 Analysis of the composite performance regarding the mechanical properties and the flame resistance

The results of both the mechanical properties and the flame retardance are separately analysed as discussed above. To be able to perform the selection process, the degree of importance of mechanical properties to Flame retardance is to be defined while taking into consideration that this depends on the application field. The decision of the weight of each share importance would be rather taken quantitatively. Combining the mechanical properties and the flame retardance in a relation would be helpful as represented in Equation 7-4. Equation 7-5 yields when assuming the ultimate tensile strength (UTS) as the mechanical property and PHRR as the flame retardance property under consideration. ‘n’ is the importance weight which lies in [0 - 1].

$$Performance\_index = (mechanical\_property)^{n} . (Flameretardance\_property)^{(1-n)}$$

Equation 7-4

$$Performance\_index = (UTS)^{n} . (PHRR)^{(1-n)}$$

Equation 7-5

Figure 7-35 shows the performance index by trying different values of 'n' at (0.33, 0.5 and 0.67). Figure 17 shows optimum around 50% ATH at the 30:70 group at any importance weight. Whereas the optimum of the 50:50 group is attained at 40% ATH only at even sharing (n=0.5) or strength biased sharing. This implies the feasibility of decreasing the ATH content to keep the mechanical properties and flame retardance as well within acceptable limits.

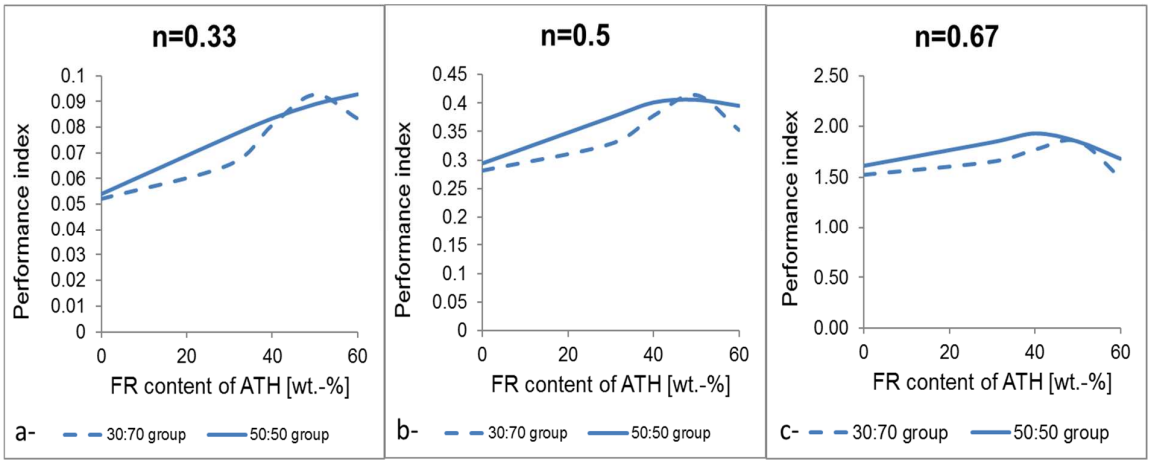


Figure 7-35: Effect of ATH content on the performance index combining the tensile strength and the flame retardance (PHRR) factors at different weights of importance

7.3.7 Outcomes

The optimisation between the mechanical and flame retardation properties for NFPC with ATH is comprehensively investigated. The recommended 60 wt.-% of ATH filler to reach V-0 class can be reduced to 40% for flax/PP composites. On the other side, the mechanical properties at 40% loading are only 7.5-12.5% negatively affected for the both investigated groups 30:70 and 50:50 respectively.

Use of fine ATH particles results in late ignition start TTI, reduced HRR and shorter ignition distinguish times (TT flame out).

UL94 results: Applying Apyral 60CD in amounts less than 30 wt.-% results in no rating, while use of 30 wt.-% helped in reaching HB rating with 0.313 mm/s. Application of 40 wt.-% or more reached V-0 class.

8 Conclusions

The study comprises different aspects of investigation in order to improve the efficiency of the NFTC composites with special focus on PP/flax system. These aspects according to section 3.1 are:

- Fibre matrix coupling (A1: Fibre treatment and coupling selection, A2: required quantity of the coupling agent).
- Compounding of natural fibres with PP (B: Temperature and shear rate with respect to the required fibre content).
- Re-processing of the NFTC granules by injection moulding parameters (C1: optimising the process parameters like injection pressure, melt temperature, mould temperature and injection speed regarding the mechanical properties, C2: Optimisation regarding flowability and fibre content accuracy, C3: Fibre content homogeneity or consistency along the injection moulded products is modelled by estimating empirical relations for both cellulose and bast fibres like hemp and flax. The model is extended to two-dimensional plate and the model results are compared to the experimental findings of fibre content after fibre extraction.)
- Functional additives to have better properties regarding (D1: impact strength and D2 & D3: fire retardance level).

The main conclusions are summarised as follows:

- A1- Selection of fibre/ Matrix treatment for coupling:

  The relatively optimum treatment combination is found through a performance index which combines the effects of the mechanical properties and water absorption as shown in Figure 8-1. This treatment is the alkalinisation of fibres with NaOH and the use of MAPP to induce the coupling between the cleaned surfaces of the flax (fibres or after fibrillation by processing) and the PP matrix. MAPP is also characterised with its availability and appropriate market price.

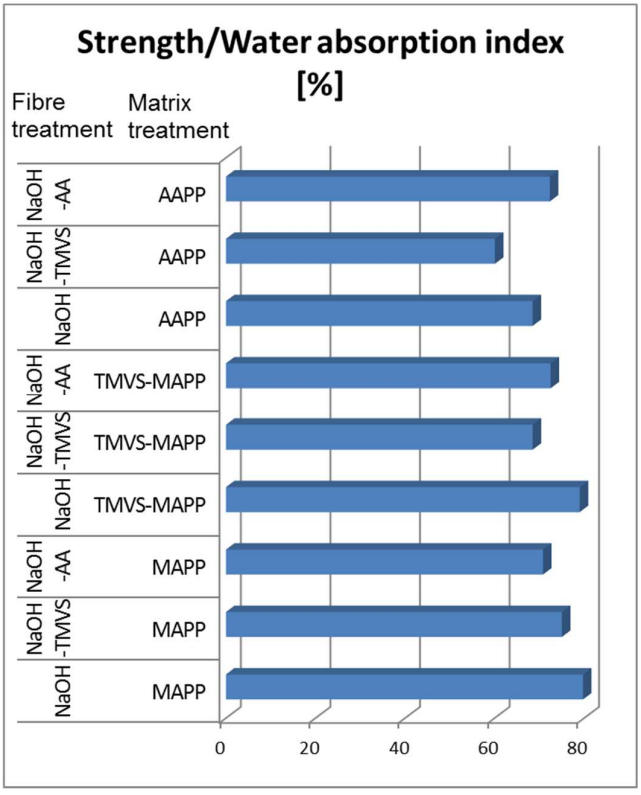


Figure 8-1: Selection chart of the suitable treatment for fibre/matrix

- A2- Optimising the alkalinisation process and the coupling agent:

  Pre-treatment of 5% NaOH for 24 days at room temperature is sufficient to have more efficient fibre surface for coupling with the thermoplastic matrix and hence further processing. The coupling agent amount is then optimised with respect to the desired natural fibre content. This is called MAPP:NF ratio.

  - The MAPP:NF ratios to get optimum E-modulus, strength and impact strength depends on natural fibre type as shown in Table 4-9. MAPP: NF ratio of 6.7% is enough for having a high improvement in mechanical properties especially in the 30% group as shown in Figure 8-2. Ratio of 1:10 of MAPP:NF (10%) however is taken as a safe percent.

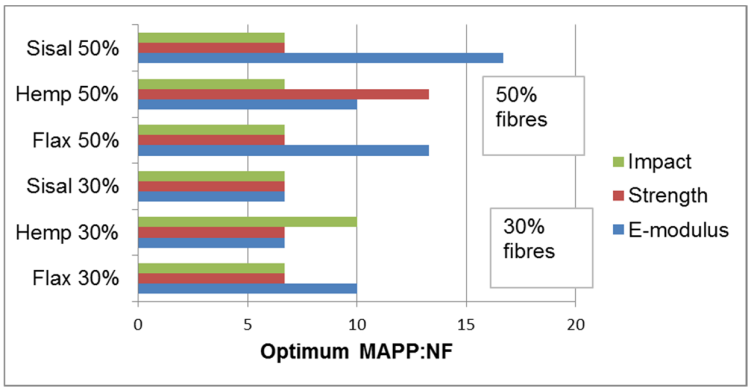


Figure 8-2: Optimum coupling agent for improving certain mechanical property

  - The effect of adding the optimum coupling agent is significant in strength and impact values as shown in Figure 8-3. This is explained in terms of the increasing probability that failure scenarios are most likely to happen in the fibre or the matrix/fibre interfaces. These failure favourite places for failure are increasing with the increase of fibres.

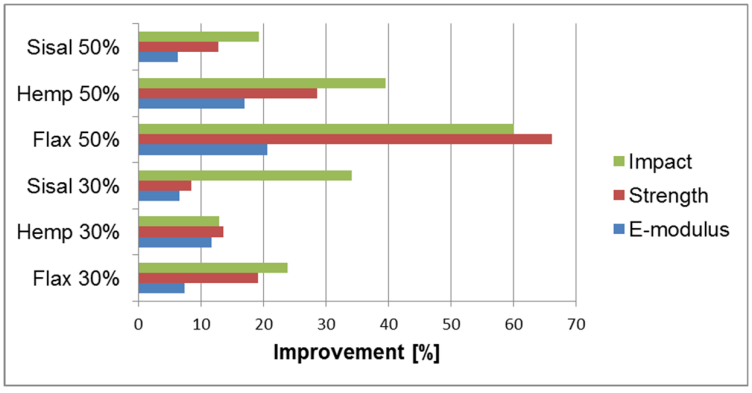


Figure 8-3: Improvement % corresponding to the optimum MAPP:NF

- B- Optimising the compounding process design and parameters for the production of NFTC granules:

- The effect of the extruder configuration proved to be significant on the fibre aspect ratio and mechanical properties of NFTC. Based on the results, it is concluded to have an extruder equipped with special elements like MPE and teeth blocks and reverse element to support back pressure. These designs allow the fibre drawing and fibrillation to avoid agglomeration of fibres as much as possible. However, further injection moulding result in reducing the effect of the extruder elements on the final properties.
- The effect of the extruder elements on the statistical distribution of fibre size is proved and the Weibull distribution parameters, describing the fibre size distribution at each extrusion element, are defined.

  The following three conclusions are inferred from the results obtained. These results are different to some common ideas about the NFTC strengthening and the extruder design:
- Improvement in E-modulus and tensile strength is explained in terms of the fibre aspect ratio, or in the available sites on the fibre surface area ready for coupling the polymer with the flax fibre. The fibre measurement supported the second reason because a great difference in aspect ratio does not show accordingly a significant effect on mechanical properties.
- The common idea of increasing strength along with the increase of the aspect ratio is not only the key player in the overall composite behaviour. Aspect ratio develops along the different elements on the extruder even with the presence of almost low shearing transport elements. This depicts that there are other factors like fibre decohesion (defibrillation) attributed to the induced temperature which influences the resulting fibre geometry.
- It is proved also that after short extrusion length, consistent aspect ratio and X90/X10 are attained without much need to the kneading elements phase. This suggests the possibility of using extruders with lower L/D ratio.

- C1- Optimising the injection moulding parameters with respect to the mechanical properties of the injected NFTC: The following ranking of significance, as in Figure 8-4, is found to affect the NFTC mechanical properties namely mould temperature, injection temperature, pressure and screw speed. For PP natural fibre composites, 180-185°C, 500 bar, 80°C and 20 m/min for temperature, pressure, mould temperature and screw speed respectively are optimum results when the mechanical properties are only considered.

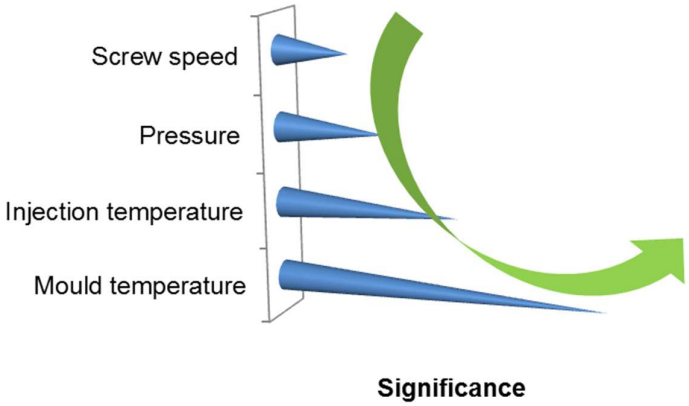


Figure 8-4: Significance of the affecting parameters on the mechanical properties of injected NFTC

- C2- Flowability and the homogeneity of fibre distribution of the injected NFTC: Change of fibre content and correspondingly fibre length in the injected NF/PP is proved. However, the consistency of the fibre content can be improved by decreasing the injection pressure and relatively by reducing the temperature. But this pressure and temperature reductions affect the flowability negatively and increase the viscosity. Fibres of non-branched with high flexural strength like cellulose show similar behaviour of superior flowability and more homogeneity of fibre content within the injection moulded products in comparison to branched low flexural strength fibres like hemp and flax.

- C3- Modelling the NFTC flowability and fibre distribution patterns: Flowability and fibre content distributions are described by empirical equations in 6.3.2. These equations are implemented in the injected two-dimensional plate. Matching between the experimental and the empirical equations is proved. However this problem should be treated analytically as a typical multiphase flow where PP and fibres are single phase regions. There is also a close trend of changing the fibre content with the fibre length as shown in Figure 8-5.

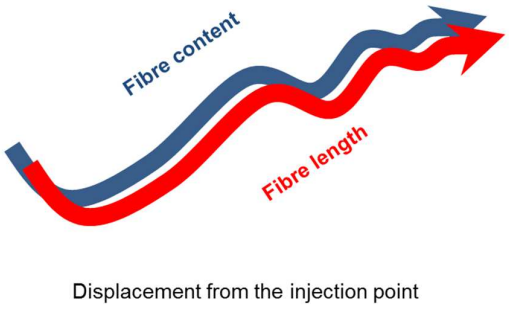


Figure 8-5: Trend of changing fibre content and fibre length

- D1- Improving the impact modifier: Impact strength improved 20 and 35% respectively with the use of nettle at 30 and 50 wt% levels of fibres. Addition of less nettle amount (10-15 wt%) fibres improves the impact strength with 11-16 wt%. Less improvement in impact strength of 8-9% is found when 10% EPDM is used at 50wt% flax. On the other side, only negative influence of triacetin was

observed on composites at any level of fibre content. Tensile strength and E-modulus: Nettle increases the tensile strength, E-modulus and elongation. while EPDM and triacetin decrease the composite tensile strength and E-modulus.

- D2- Influence of flame retardants: DECA or DECA/ Sb_2O_3 show the best flame retardance level as well as the mechanical properties. But DECA, is not considered due to the healthy regulations. Ammonium polyphosphate has a remarked performance at 26% to reach V0 class but with 29% loss in strength. Nanoclays with 3% of nanoclays in synergism with ammonium polyphosphate reaches the V0 class. Implementation of 30% mineral FR Magnesium hydroxide attained HB-class with a loss in UTS around 30%. A material selection tool is developed for a compromise between mechanical properties and flame retardance as shown in Figure 7-26.

- D3- Optimisation of flame retardant regarding the mechanical properties: It is feasible to apply lower mineral FR (ATH), namely 40%, without losing the V-0 class and the drop in mechanical properties at this 40% is minimised to only 7.5-12.5% for the both investigated groups 30:70 and 50:50 of Flax:PP respectively.

9 Outlook

Recalling the main problems stated in the problem definition section 1.2, the study tackles the following problems:

- Problem of low impact strength for PP/flax composite is studied using different techniques (plasticizer, elastomeric rubber and hybridisation with other fibres): Although the measured enhancement of the impact strength in the trials made in this study, the improvement is not enough to be compared with the glass fibre composites. This problem represents the most important barrier to the market of NFTC. Further research regarding chemical treatments is needed till a balance is found between the impact strength, the tensile strength and the production costs.
- Controlling the shear compounding process like extrusion for natural fibres and thermoplastics by defining and optimising the process parameters: The study is limited to certain type of fibre (flax). The study points also to the effect of the extruder elements on the final properties. The results claim that the lower L/D ratio can be used. This claim needs to be tested in future work.
- Incomplete database about the impact modifiers and flame retardants of NFTC products: A review of different flame retardants with different fibre types and fibre contents is tried. However more future studies are needed to investigate the synergism between some of these flame retardants such as mineral inorganic hydrates ATH, APP, nanoclays, zink borate…
- Controlling the flow behaviour of NFTC in injection with respect to the fibre content distribution and hence the mechanical properties: A trial is made in this study to model the flowability and fibre distribution empirically. However an analytical study is needed to include factors such as:
  - Temperature on fibre fragmentation or splitting (fibrillation),
  - Flexure of fibres. However the mechanistic models, if used, should be compromised with the computation burden,
  - Branching of fibres.

Future work should include the widening of the NFTC market by breaking the limits of polyolefines. Engineering plastics with their challenging requirements of high compounding temperature will increase the added value of NFTC. Some actual studies are trying to open such a door [El-14b].
The way of understanding the NFTC behaviour during flowing and loading is still too challenging. However, by the increasing development, the benefits will not be limited for the plastics industry but also for other fluid flow problems with engineering and non-engineering aspects such as the flow dynamics of injections into blood through vessel walls.

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Appendix

Table A- 1. Mechanical properties of composites at different MAPP:NF ratios, fibre type and MAPP type at 30% and 50% fibre content

Fibre	Fibre [%]	MAPP/NF [%]	MAPP type	Stiffness [MPa]	Dev. [MPa]	UTS [MPa]	Dev. [MPa]	Elongation [%]	Dev. [%]	Impact [kJ/m²]	Dev. [kJ/m²]
Copolymer content and fibre type effect at 30% fibre											
Flax	30	0		5221,05	494,12	36,03	2,78	4,54	1,21	6,21	0,51
Flax	30	6,7	Type (A)	5420,14	351,10	42,85	0,62	4,06	0,51	7,69	0,77
Flax	30	10	Type (A)	5631,40	502,80	43,06	0,94	4,30	0,74	7,40	0,61
Flax	30	13,3	Type (A)	5524,36	409,90	43,17	0,95	3,16	0,52	6,76	0,84
Flax	30	16,7	Type (A)	5598,67	405,09	42,22	1,33	3,73	0,89	7,04	0,59
Hemp	30	0		5129,19	226,66	37,81	0,98	3,47	0,81	6,30	0,42
Hemp	30	6,7	Type (A)	5728,05	231,07	43,07	0,99	3,34	0,55	6,14	1,23
Hemp	30	10	Type (A)	5608,72	180,15	42,94	1,06	3,11	0,28	7,00	0,58
Hemp	30	13,3	Type (A)	5457,25	80,90	43,59	0,89	3,03	0,15	6,41	0,24
Hemp	30	16,7	Type (A)	5583,79	639,65	41,67	2,33	3,21	0,56	6,24	0,64
Sisal	30	0		4665,05	409,03	36,64	1,52	3,65	0,84	5,27	0,66
Sisal	30	6,7	Type (A)	5202,80	198,51	39,06	0,86	4,72	0,64	7,07	0,34
Sisal	30	10	Type (A)	5205,86	247,57	38,87	1,35	3,49	0,60	6,03	0,75
Sisal	30	13,3	Type (A)	4960,82	331,74	38,82	1,29	4,37	0,28	6,30	0,62
Sisal	30	16,7	Type (A)	5227,98	394,62	38,15	0,46	4,44	0,63	6,84	0,41
Copolymer content and fibre type effect at 50% fibre											
Flax	50	0		6886,97	686,22	30,69	1,61	3,21	0,53	4,33	0,67
Flax	50	6,7	Type (A)	7853,07	809,74	51,40	1,83	2,68	0,40	6,89	0,51
Flax	50	10	Type (A)	8028,76	595,67	50,89	1,29	2,24	0,31	6,86	0,42
Flax	50	13,3	Type (A)	8308,41	274,37	51,47	1,23	2,09	0,14	6,44	0,17
Flax	50	16,7	Type (A)	8158,28	864,52	48,63	2,42	1,97	0,36	5,69	0,75
Hemp	50	0		7327,36	351,78	41,64	0,85	1,77	0,28	4,37	0,42
Hemp	50	6,7	Type (A)	7877,77	472,21	50,84	1,78	2,04	0,15	6,01	0,41
Hemp	50	10	Type (A)	8575,48	537,46	51,39	0,92	1,57	0,18	5,73	0,76
Hemp	50	13,3	Type (A)	8403,05	650,52	53,47	0,93	1,97	0,39	6,01	0,37
Hemp	50	16,7	Type (A)	8475,31	354,92	51,29	1,58	1,83	0,30	5,46	0,45
Sisal	50	0		7592,66	327,48	43,96	1,38	2,71	0,66	6,04	0,55
Sisal	50	6,7	Type (A)	7677,89	243,29	49,58	0,94	2,29	0,38	7,20	0,77
Sisal	50	10	Type (A)	7609,82	320,35	48,69	1,31	2,44	0,33	6,79	0,60
Sisal	50	13,3	Type (A)	7643,92	1048,20	50,11	1,21	1,87	0,10	5,97	0,48
Sisal	50	16,7	Type (A)	8076,00	646,00	47,47	1,61	1,71	0,26	6,20	0,70
Copolymer content and type effect at 30%											
Flax	30	0		5221,05	494,12	36,03	2,78	4,54	1,21	6,21	0,51
Flax	30	6,7	Type (A)	5420,14	351,10	42,85	0,62	4,06	0,51	7,69	0,77
Flax	30	10	Type (A)	5631,40	502,80	43,06	0,94	4,30	0,74	7,40	0,61
Flax	30	13,3	Type (A)	5524,36	409,90	43,17	0,95	3,16	0,52	6,76	0,84
Flax	30	16,7	Type (A)	5598,67	405,09	42,22	1,33	3,73	0,89	7,04	0,59
Flax	30	0		5221,05	494,12	36,03	2,78	4,54	1,21	6,21	0,51
Flax	30	6,7	Type (B)	5118,36	185,38	41,74	0,40	4,73	0,67	7,61	0,64
Flax	30	10	Type (B)	5102,93	106,19	43,55	0,53	5,26	0,93	8,50	1,11
Flax	30	13,3	Type (B)	5100,00	410,98	45,11	1,51	5,41	1,34	8,50	0,77
Flax	30	16,7	Type (B)	4972,26	371,62	43,66	0,82	6,11	0,60	9,66	0,76
Copolymer content and type effect at 50%											
Flax	50	0		6886,97	686,22	30,69	1,61	3,21	0,53	4,33	0,67
Flax	50	6,7	Type (A)	7853,07	809,74	51,40	1,83	2,68	0,40	6,89	0,51
Flax	50	10	Type (A)	8028,76	595,67	50,89	1,29	2,24	0,31	6,86	0,42
Flax	50	13,3	Type (A)	8308,41	274,37	51,47	1,23	2,09	0,14	6,44	0,17
Flax	50	16,7	Type (A)	8158,28	864,52	48,63	2,42	1,97	0,36	5,69	0,75
Flax	50	0		6886,97	686,22	30,69	1,61	3,21	0,53	4,33	0,67
Flax	50	6,7	Type (B)	7115,11	281,97	48,56	0,88	2,13	0,41	6,97	0,80
Flax	50	10	Type (B)	7707,53	556,67	51,77	1,89	2,24	0,44	7,31	0,57
Flax	50	13,3	Type (B)	7904,50	678,93	54,41	1,66	2,53	0,26	7,30	0,95
Flax	50	16,7	Type (B)	7606,82	700,45	57,37	1,05	2,57	0,61	7,43	1,56

Table A- 2. Mechanical properties of the hot pressed samples out of extrusion

Extruder	Theoretical fibre content [wt.-%]	Speed [rpm]	E-modulus [MPa]	Standard deviation [MPa]	Ultimate tensile strength	Standard deviation [MPa]	Strain at break [%]	Standard deviation [%]
A	10	100	753.1	138.3	16.04	2.400	3.64	0.79
A	20	100	1327.0	140.3	21.20	2.523	2.31	0.73
A	30	100	964.3	215.1	19.81	4.817	2.13	0.83
A	10	200	786.8	205.0	19.12	3.676	4.90	2.43
A	20	200	655.8	157.1	13.98	1.755	2.96	0.92
A	30	200	1227.0	252.3	18.58	5.139	1.74	0.69
A	10	300	762.4	164.2	16.21	2.793	4.25	0.9
A	20	300	963.0	237.5	19.09	4.348	3.36	0.75
A	30	300	1025.0	184.4	16.33	5.103	1.54	0.82
B	10	100	782.2	94.52	16.27	3.039	3.78	1.77
B	20	100	495.7	84.26	15.22	4.342	3.56	0.96
B	30	100	1003.0	256.1	19.62	5.693	3.01	0.90
B	10	200	700.0	100.0	11.19	2.247	4.31	1.33
B	20	200	489.9	130.6	11.69	1.985	4.48	1.33
B	30	200	960.1	226.0	16.94	3.178	2.39	0.83
B	10	300	651.4	163.8	15.56	4.924	4.44	1.18
B	20	300	577.9	168.1	12.70	3.867	3.17	1.12
B	30	300	824.4	230.1	15.96	4.222	1.87	0.48
C	10	100	1354.0	282.2	28,41	5.316	3.58	1.01
C	20	100	1435.0	356.2	32,91	7.539	2.27	1.30
C	30	100	1515.0	127.4	26,32	4.040	2.35	0.84
C	10	200	1140.0	364.9	22,09	2.997	2.70	2.01
C	20	200	1435.0	356.2	26,33	7.539	2.27	1.30
C	30	200	1603.0	398.2	24,64	6.715	1.94	0.59
C	10	300	1515.0	153.4	23,45	5.137	3.62	0.42
C	20	300	1435.0	87.7	25,6	2.698	2.37	0.80
C	30	300	1603.0	398.2	24,64	6.715	1.94	0.59
D	10	100	1039.0	56.16	26.17	1.192	4.00	0.64
D	20	100	989.2	230.7	17.77	8.395	3.40	0.68
D	30	100	1421.0	246.1	21.47	1.084	2.16	0.79
D	10	200	1037.0	150.4	21.58	3.098	3.60	0.82
D	20	200	989.2	230.7	17.77	8.395	3.40	0.68
D	30	200	1264.0	247.3	20.89	3.887	1.95	0.55
D	10	300	1235.0	221.3	24.05	4.522	2.97	1.25
D	20	300	1101.0	287.4	16.86	8.061	2.76	0.60
D	30	300	1150.0	276.8	20.38	5.019	2.29	0.55

Table A- 3. Qicpic measurements and statistical analysis of fibre dimensions at 30% Wf and 200 rpm for the all studied extruders (A, B, C and D)

Extruder	Position [mm]	Number of fibres	Diameter/ Length [µm] x(10%)	Diameter/ Length [µm] x(50%)	Diameter/ Length [µm] x(90%)	X90/X10 Regarding length	AR
A	113,33	543	5,61/40,02	10,69/218,40	26,11/1579,88	39,48	20,43
A	140,00	5452	5,60/38,18	11,38/217,67	25,01/2475,40	64,83	19,12
A	200,00	7071	5,52/36,73	9,73/197,14	49,80/1857,82	50,58	20,26
A	246,67	7351	5,50/37,12	9,58/225,96	48,48/2607,05	70,23	23,59
A	280,00	5697	5,58/39,66	10,18/340,56	51,97/3729,22	94,03	33,45
A	306,67	11537	5,54/38,42	9,84/263,74	19,83/2141,19	55,73	26,80
A	440,00	6394	5,60/36,67	10,31/167,94	22,60/1425,76	38,88	16,29
A	460,00	9645	5,55/36,74	9,92/181,38	19,92/1376,46	37,46	18,28
A	473,33	6998	5,62/36,95	10,59/179,04	23,96/1373,29	37,17	16,91
A	646,00	1865	5,27/22,49	9,99/117,00	18,53/776,48	34,53	11,71
B	126,67	7510	5,49/42,78	9,52/201,94	20,34/4554,01	106,45	21,21
B	146,67	8042	5,56/37,13	10,09/231,51	20,67/2599,25	70,00	22,94
B	266,67	14181	5,55/37,09	9,89/210,25	19,55/1695,09	45,70	21,25
B	293,30	11616	5,62/38,25	10,40/237,90	20,44/3415,88	89,30	22,88
B	400,00	14553	5,55/36,37	9,90/167,92	19,34/1346,24	37,02	16,96
B	426,67	25557	5,59/36,44	10,26/164,77	19,71/1229,71	33,75	16,06
B	646,00	10895	5,65/22,47	10,78/129,38	20,69/938,10	30,38	12,00
C	113,33	7481	5,68/40,31	19,43/443,11	20,35/2445,74	60,67	22,78
C	126,67	3691	5,49/38,02	20,62/422,12	20,30/2330,09	61,29	20,47
C	153,33	1455	5,50/37,25	15,75/363,73	20,21/2007,82	53,90	23,09
C	166,67	2311	5,47/36,35	13,26/304,96	20,08/1928,32	53,05	22,99
C	193,67	981	5,39/36,11	12,18/249,98	20,03/1838,21	50,91	20,52
C	206,67	765	5,40/35,01	12,16/233,83	20,08/1754,82	50,12	19,23
C	233,33	1487	5,40/33,19	10,70/223,53	20,00/1683,38	50,72	20,89
C	246,70	3647	5,51/34,10	12,47/219,61	19,97/1379,93	40,47	17,62
C	393,30	2557	5,39/35,08	14,82/211,48	20,10/1290,72	36,79	14,27
C	420,00	608	5,31/33,89	12,93/203,87	19,95/1233,91	36,41	15,77
C	433,30	1287	5,29/33,24	12,29/203,74	19,90/1212,24	36,47	16,58
C	453,30	1378	5,28/35,14	10,76/200,40	19,88/1167,36	33,22	18,63
C	646,00	21633	5,64/36,79	10,69/170,50	19,83/1117,80	41,57	15,95
D	113,33	5899	5,50/39,04	9,65/371,09	19,55/3558,90	91,16	38,45
D	166,67	4055	5,50/36,19	9,63/170,68	18,86/1353,81	37,41	17,72
D	206,67	600	13,83/20,69	9,65/108,68	18,78/693,13	33,50	11,26
D	246,67	7945	13,77/22,08	9,66/157,47	18,87/1027,90	46,55	16,30
D	380,00	18632	13,98/22,00	10,32/127,39	19,90/906,71	41,21	12,34
D	413,30	4980	13,86/35,90	9,91/149,16	18,83/1282,17	35,71	15,05
D	433,30	10482	10,35/21,63	9,60/132,96	18,27/939,77	43,45	13,85
D	446,67	10486	5,56/22,42	9,99/149,21	18,82/932,08	41,57	14,94
D	446,67	7460	5,48/21,12	9,45/136,64	18,63/789,39	37,38	14,46
D	646,00	21037	5,28/21,68	10,02/127,66	18,59/780,23	35,99	12,74

Table A- 4. Mechanical results of the NFTC samples listed in Table 6-1

sample #	E-modul [MPa]	Stand. Dev. [MPa]	Tensile strength [MPa]	Stand. dev. [MPa]	Elongation [%]	Stand. dev. [%]	Impact strength [KJ/m²]	Stand. dev. [kJ/m²]
1	2150	104	29.2	0.737	5.4	0.29	10.8	0.75
2	2170	111	29.8	0.645	5.7	0.84	11.6	0.61
3	2240	44.7	31.3	0.581	5.2	0.3	11.4	1.18
4	2270	57.7	30.7	0.98	5.3	0.75	10.9	1.38
5	2030	104	28.7	1.26	5.8	0.79	11.5	0.96
6	1930	106	28.65	1.11	6.5	0.82	13.7	1.07
7	1987	130	27.9	1.14	5.4	0.86	12.1	1.44
8	1993.3	58.59	30.2	0.264	5.61	0.77	12.6	1.52
9	1890	145	28.6	0.507	5.8	0.74	13	1.31
10	1923	203	27.8	0.5	5	0.54	12.5	1.43
11	2120	56	29.9	0.686	5.3	0.44	12.7	0.71
12	2060	59.3	28.9	1.44	4.9	0.47	10.9	1.41
13	1940	32.3	27.8	0.419	5.1	0.51	13.7	0.66
14	2023.3	20.82	27.6	0.683	4.54	0.34	12.5	1.35
15	2130	82.7	29.4	0.357	4.6	0.63	11.1	1.134
16	2080	69.6	29	0.381	5.1	0.8	10.1	0.62
17	2010	99.8	28.3	0.224	5.3	0.7	10.6	0.42
18	1930	139	27.2	1.02	5.4	0.39	12.9	0.62
19	1900	88.3	27.3	0.548	5.5	0.43	10.3	0.95
20	2120	111	29.1	0.524	5.0	0.46	10.1	0.78

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3. "Processing and modelling of the mechanical behavior of natural fiber thermoplastic composite: Flax/Polypropylene", A. Elsabbagh, L. Steuernagel and G. Ziegmann, Polymer Composites, Vol 30, Issue 4, April 2009, 510-519
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Curriculum Vitae

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